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PROPERTIES OF ENAMEL SLIPS: I, GENERAL PROPERTIES OF CLAYS AND ENAMEL SLIPS*

By Burnham W. King, Jr., Herbert D. Carter, and Harry C. Draker

Abstract

Five clays used to suspend porcelain enamels and their properties were studied. Fundamental data were first obtained on the clays, which were then milled in different proportions with several types of porcelain enamel frits. The properties of the resulting slips were studied. The pickup weight, that is, the amount of enamel retained on a ground-coated plaque which had been dipped in the slip and allowed to drain, was used as a basis of comparison.

I. Introduction

The object of this study was to determine the properties of five typical enameling clays and to investigate the action of these clays when milled with various types of enamel frits. The data obtained on the clays include crystal form, particle size, hydrogen-ion concentration, carbon content, and weight loss on heating. The pickup characteristics of enamel slips were compared for individual clays as well as for several clay combinations at different specific gravities and times of aging. The pickup weight was found by dipping a plaque in the enamel slip, allowing it to drain, drying, and then weighing to determine the amount of dried enamel retained.

Clays were selected that were known to work well in enamels and could be roughly classified as follows: Two of the clays, A and B, gave low set and produced considerable opacity when fired in enamels; clay C was intermediate as to set and opacity; clays D and E gave high set and very little opacity in fired enamels.

II. Properties of Typical Enameling Clays

(1) Physical Properties

Two important physical properties which might have a bearing on the action of various clays in enamel slips are mineralogical constitution and particle size, and these properties were investigated.

(*A*) *Mineral Type:* X-ray patterns were taken of the five clays, and the interplanar spacings as determined from these patterns were compared with the published data on the clay minerals.[1] Clays A, B, D, and E were found to be largely of the kaolinite type although they all contained considerable quartz. The amount of quartz was probably larger in clays A and B than in D and E. Clay C was a somewhat different type in that along with the kaolinite and quartz it also possessed a large quantity of illite. X-ray patterns of the five clays are shown in Fig. 1.

(*B*) *Particle Size:* From the X-ray patterns, the clay minerals and the quartz in sample C appeared to be very fine grained. The quartz in the other clays, in comparison, was relatively coarse. Settling tests were made to give some measure of the relative particle sizes. In making these tests, the clays were mixed with water and a little tetrasodium-pyrophosphate for a dispersing agent as recommended by Loomis.[2] The clay-water mixtures were first allowed to stand for two weeks. The supernatant liquid was then removed, dried, and the amount of solids which had remained in suspension was determined. This procedure was repeated for a 17-hour and a 1-hour settling period. The maximum particle diameter was then calculated according to Stokes' law of settling. The results are given in Table I.

(2) Chemical Properties

To get some idea of the chemical properties that might be of interest in enameling, several tests were performed on the clays.

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (Enamel Division). Received June 29, 1944.

[1] (*a*) P. F. Kerr, "Decade of Research on Nature of Clay," *Jour. Amer. Ceram. Soc.*, **21** [8] 267–86 (1938).

(*b*) R. E. Grim and W. F. Bradley, "Investigation of Effect of Heat on Clay Minerals Illite and Montmorillonite," *ibid.*, **23** [8] 242–48 (1940).

(*c*) C. G. Harman and F. Fraulini, "Properties of Kaolinite as Function of Particle Size," *ibid.*, **23** [9] 253–59 (1940).

(*d*) Lane Mitchell and E. C. Henry, "Nature of Georgia Kaolins, I–II," *ibid.*, **26** [4] 105–19 (1943).

[2] G. A. Loomis, "Grain Size of Whiteware Clays as Determined by the Andreasen Pipette," *ibid.*, **21** [11] 393–99 (1938).

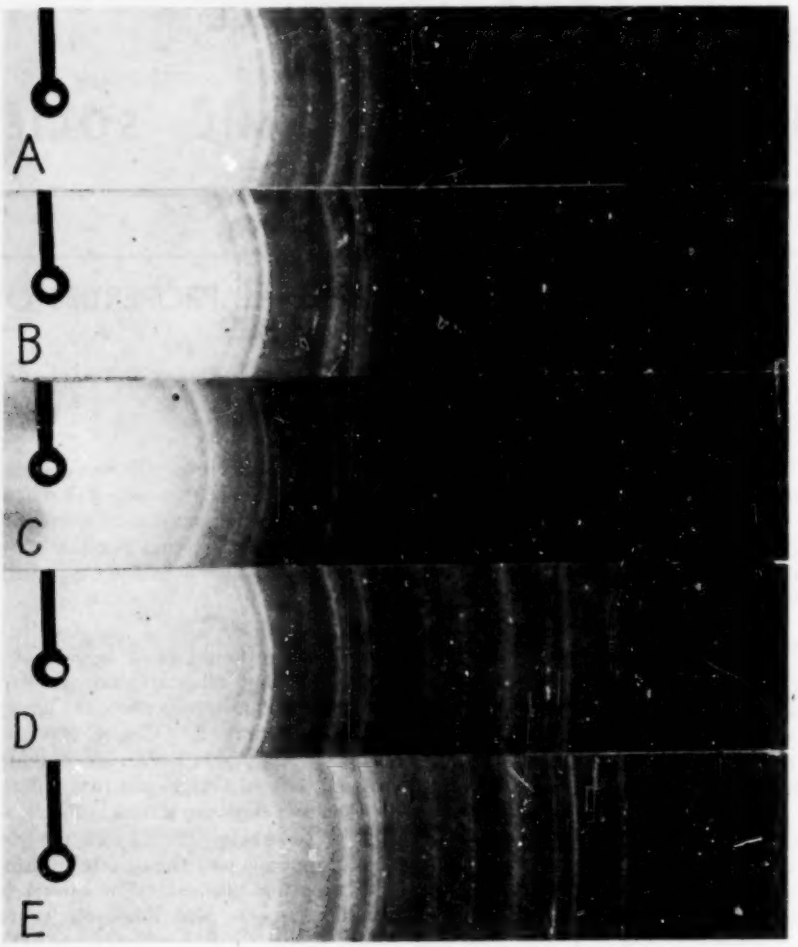

FIG. 1.—X-ray patterns of clays.

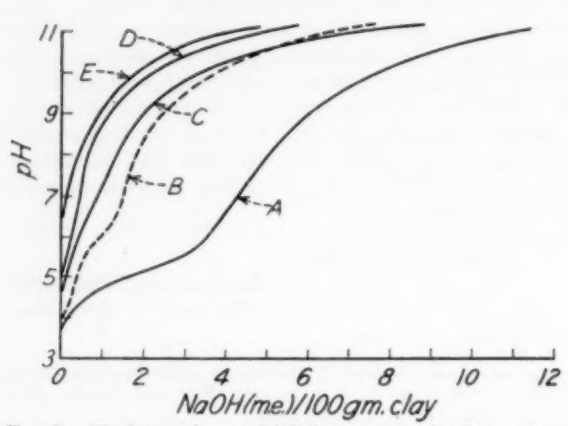

FIG. 2.—Hydrogen-ion vs. NaOH concentration for various clays.

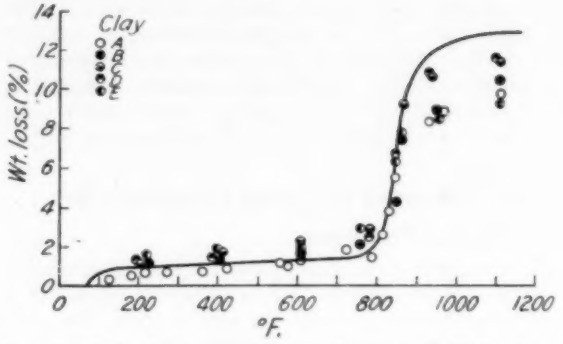

FIG. 3.—Dehydration of clays; data on kaolinite from Harman.[3]

(*A*) *Hydrogen-Ion Data:* The pH values of the different clays were determined as follows: One part of clay was added to 7 parts of water, and the mixture was titrated with $^1/_{10}N$ NaOH using a Beckmann pH meter. This clay-water ratio would correspond, for example, to a mill addition of 6 parts of clay and 42 parts of water per 100 parts of frit. The results are given in Fig. 2. The curves show a variation in the initial electrolyte content of the clays as indicated by the initial difference in pH. Differences in the possible buffering action of the various clays is also indi-

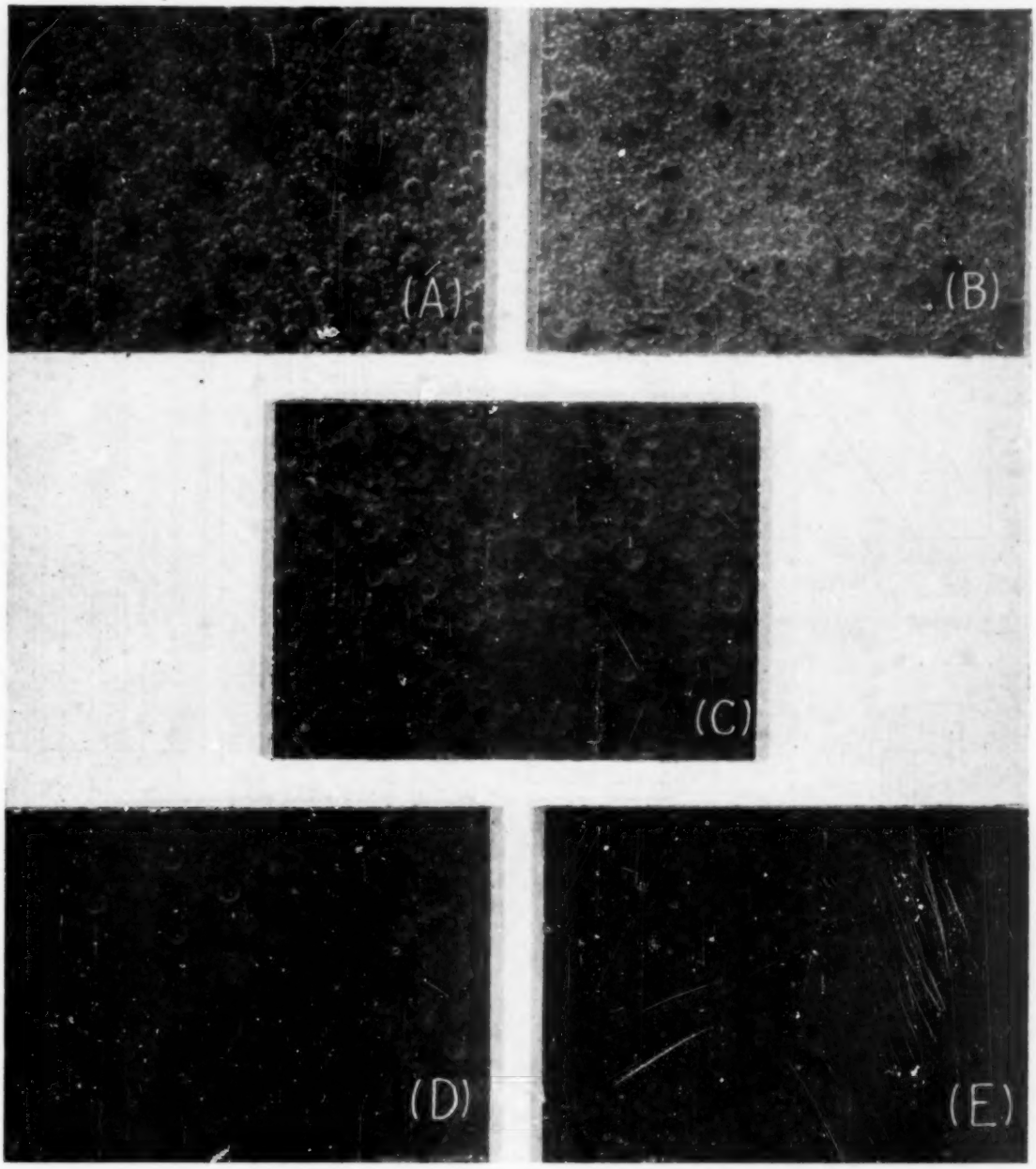

FIG. 4.—Clays milled with clear frit and fired; × 100.

TABLE I

SETTLING TESTS OF CLAYS

Clay	Percentage of clay of various maximum particle diameter (μ)			
	0.7	2.0	4.0	Unlimited
A	44.6	24.3	20.2	10.9
B	62.3	25.0	10.9	1.8
C	59.3	24.0	12.5	4.2
D	44.8	31.7	14.3	9.2
E	54.0	22.3	12.3	11.4

cated by the differences in the shape of these curves.

(*B*) *Weight Loss on Heating:* The clays were heated in an electric furnace and the loss in weight was determined. These data are plotted in Fig. 3 along with that of kaolinite as published by Harman.[3] The clays all appear quite similar in this test, even clay C which was known to contain some illite. It is to be expected that the maximum weight losses should

[3] C. G. Harman, "Clay Technology as Applied to Enamels," *Proc. Porcelain Enamel Inst. Forum, Fifth Forum, Oct., 1940*, pp. 20–25; *Ceram. Abs.*, **20** [4] 84 (1941).

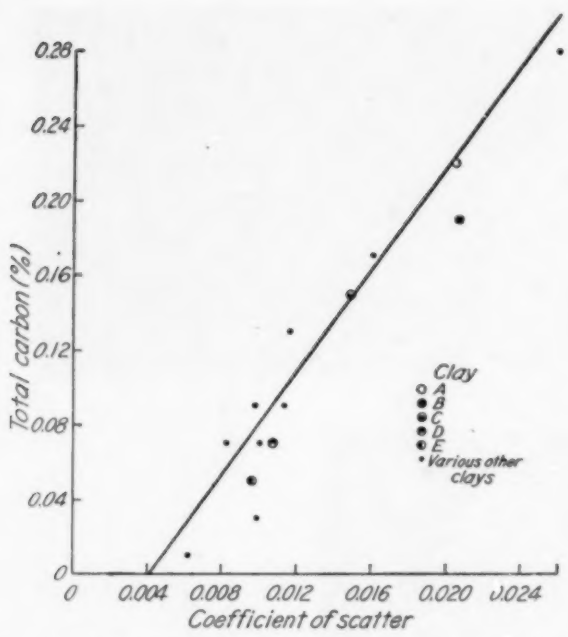

FIG. 5.—Carbon content of clay vs. scattering coefficient of fired enamel.

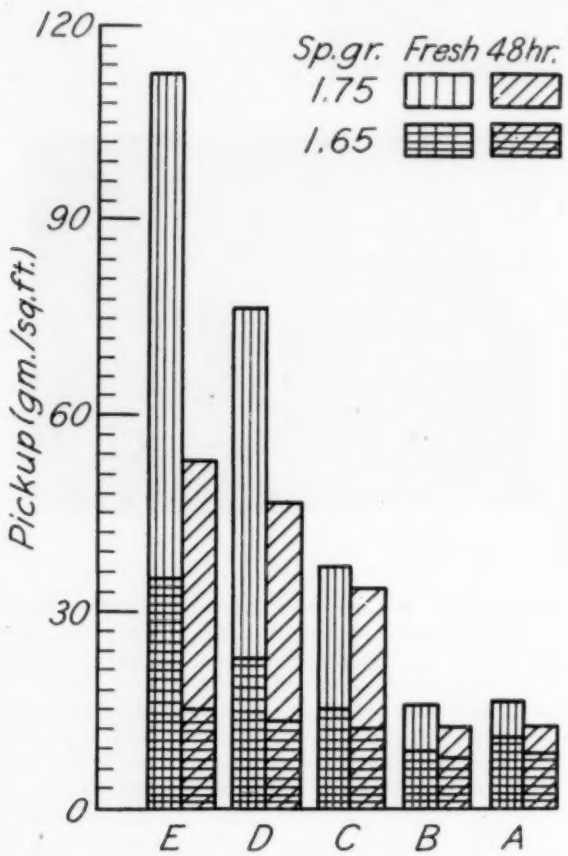

FIG. 6.—Pickup clays vs. frit A pickled plaques.

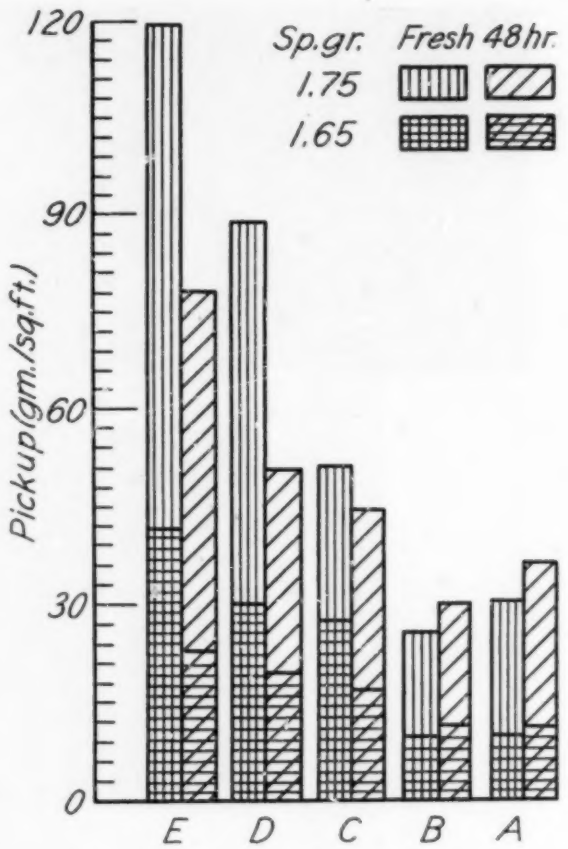

FIG. 7.—Pickup clays vs. frit B pickled plaques.

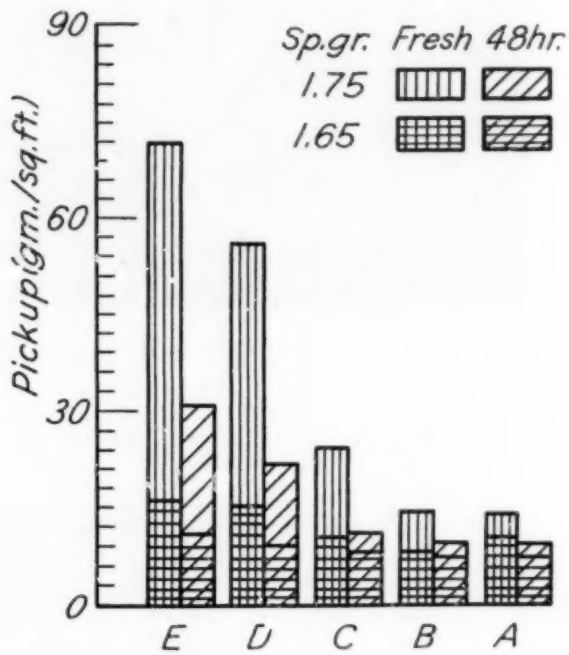

FIG. 8.—Pickup clays vs. frit C pickled plaques.

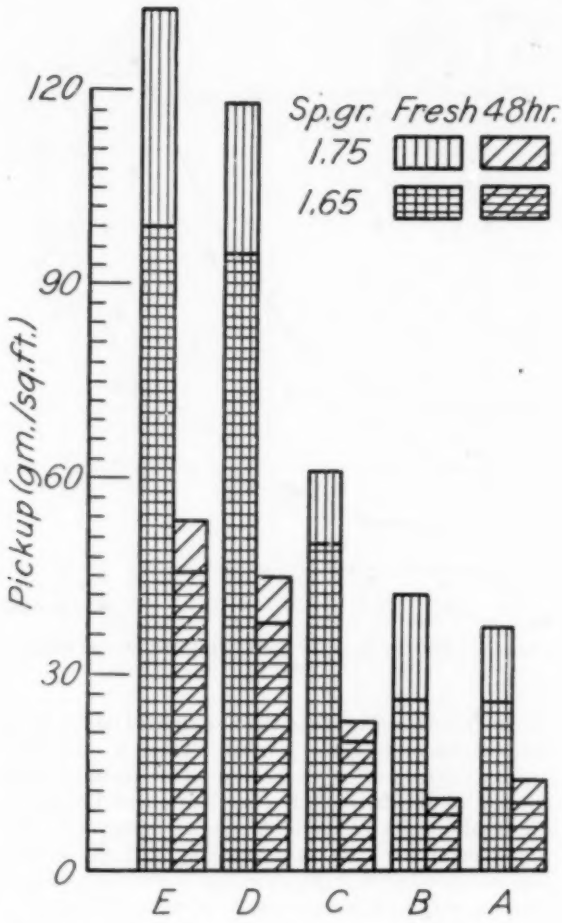

FIG. 9.—Pickup clays vs. frit D ground-coat plaques.

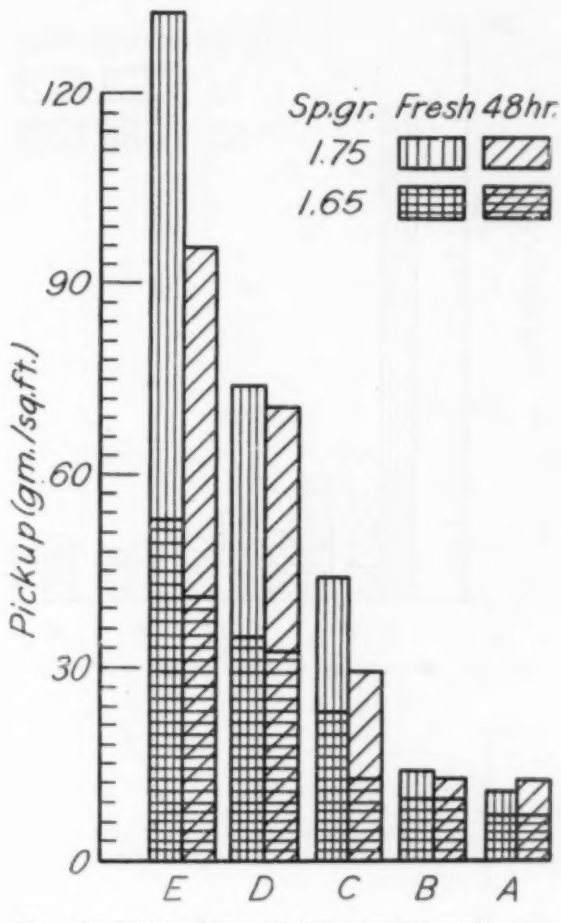

FIG. 10.—Pickup clays vs. frit E ground-coat plaques.

be less than the values for pure kaolinite because of the amount of quartz present. As shown by the X-ray patterns, these clays probably contained between 15 and 30% of the latter material. There seemed to be no direct relationship between the weight loss of these clays and their bubble structure as measured by the amount of opacity which they contributed to a clear frit.

(*C*) *Total Carbon:* The total carbon content of the raw clays was determined by combustion and absorption of the CO_2 evolved. These determinations were made in an attempt to find some definite factor that would yield a correlation with the bubble structure given an enamel by the various clays. The results are given in Table II.

III. Properties of Clays in Fired Enamels

When a frit is milled with a clay and fired, the bubble structure of the resulting enamel may vary considerably, depending on the type of clay used. The clays used in this investigation had a wide variation in opacity as shown in Table II. This table gives the reflectance at two weights of application and the corresponding scattering factors for the clays when milled with a clear frit and fired. The following mill addition was used: frit 100, clay 7, light magnesium carbonate 0.1, and water 40 to 42.5 parts.

The photomicrographs shown in Fig. 4 were taken of the fired enamels at a magnification of 100 diameters. As the ground-coat enamel was a dark blue, the difference in the opacity contributed by the different clays is quite apparent. Clays, such as A and B, which produce many fine bubbles, render an enamel more opaque than do clays D and E, which produce only a few large bubbles.

The primary source of the bubbles is apparently the carbon in the clay. Figure 5 shows that the scattering

TABLE II

CARBON CONTENT AND OPACITY OF CLAYS

Clay	Total carbon content (%)	Reflectance (%)		Coeff. of scatter
		40 gm./ft.^{2}	100 gm./ft.^{2}	
A	0.19	32.9	53.6	0.0206
B	0.22	31.7	53.5	0.0204
C	0.15	24.8	45.7	0.0149
D	0.07	18.0	38.0	0.0107
E	0.05	16.9	35.8	0.0096

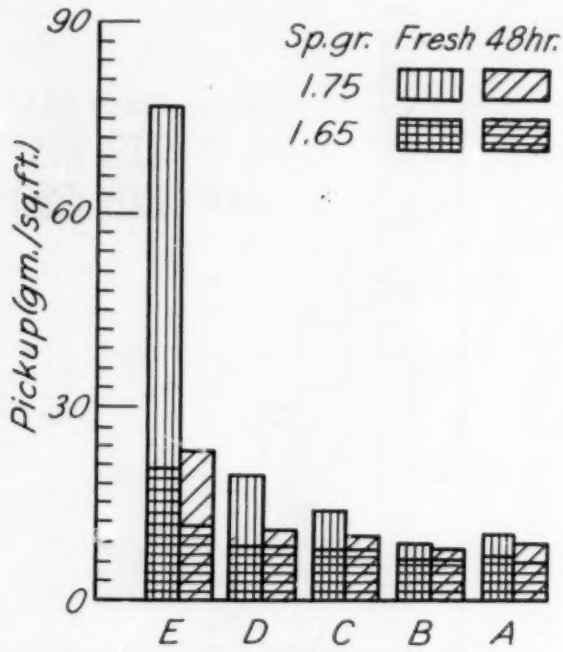

FIG. 11.—Pickup clays vs. frit F ground-coat plaque.

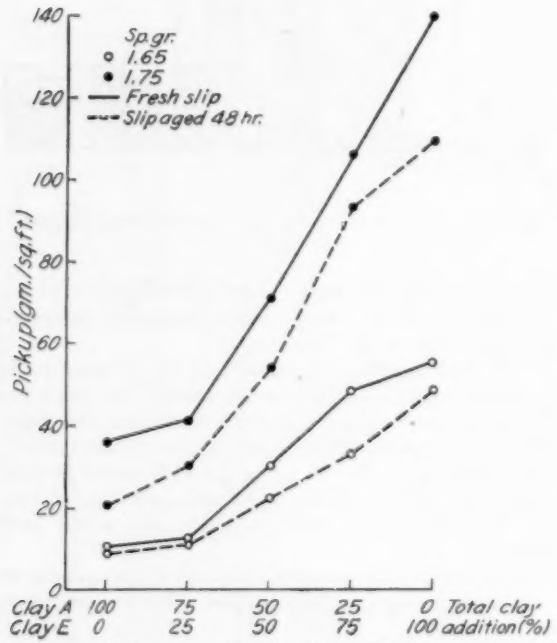

FIG. 12.—Pickup vs. clay blend for frit D and clays A and E.

factor[4] for the fired enamel is approximately proportional to the carbon content of the clay. Data are included for other clays than the five studied to show that this conclusion is fairly general. There is, of course, some scattering at zero carbon content because of the opacity of the frit. This contribution of the frit to the total opacity of the fired enamel, however, is relatively small. It is rather surprising that the correlation is as good as that shown in Fig. 5 when it is realized that the carbon in the clay may be present in any of a variety of different forms. These include carbonates, organic material, graphite, or any of the various forms of carbon or carbon compounds to be found in coal.

[4] (*a*) P. Kubelka and F. Munk, "Ein Beitrag zur Optik der Farbenstriche," *Z. Tech. Physik.*, **12**, 593 (1931).
(*b*) B. W. King, Jr., "Effect of Particle Size and Index of Refraction on Reflectance," *Jour. Amer. Ceram. Soc.*, **23** [8] 221–25 (1940).

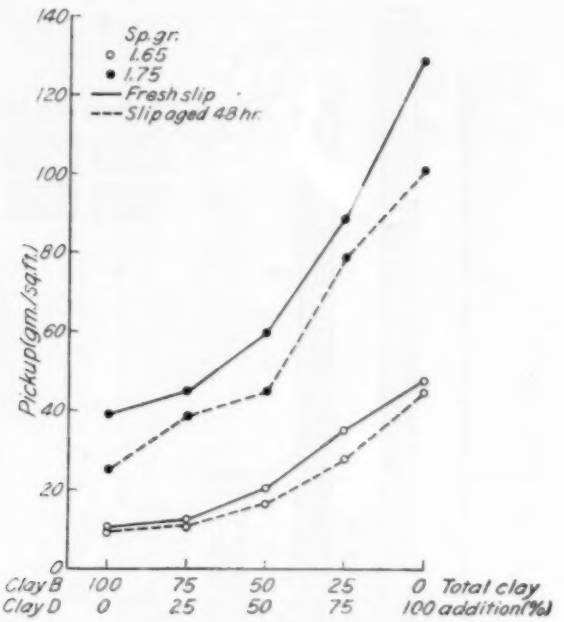

FIG. 13.—Pickup vs. clay blend for frit D and clays B and D.

IV. Properties of Clays in Enamel Slips

(1) Single Clays

In investigating the action of clays when milled with frit and water, it was decided to use the following types of frits that were known to give a wide range of soluble salts in the mill liquor:

Frits A and B, readily fusible ground coat
Frit C, moderately refractory ground coat
Frit D, ordinary opaque antimony cover coat
Frit E, clear cover coat with class A acid resistance
Frit F, zirconia-opacified cover coat

Frits A and B, although firing at about the same temperature, were known to contribute different soluble salts to the mill liquor. The following mill addition was used with all the frits so that the results would be comparable: Frit 100, clay 7, and water 42.5 parts.

In making the pickup tests, 4- by 6-in. plaques were used; those for the ground-coat slips were pickled steel and those for the cover-coat slips were steel covered with fired ground coat. After the plaques had been dipped in the enamel slip, they were allowed to drain in a vertical position until all flow had ceased.

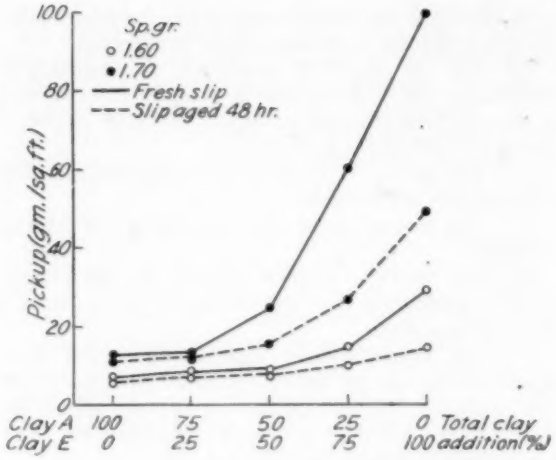

FIG. 14.—Pickup vs. clay blend for ground-coat slip and clays A and E.

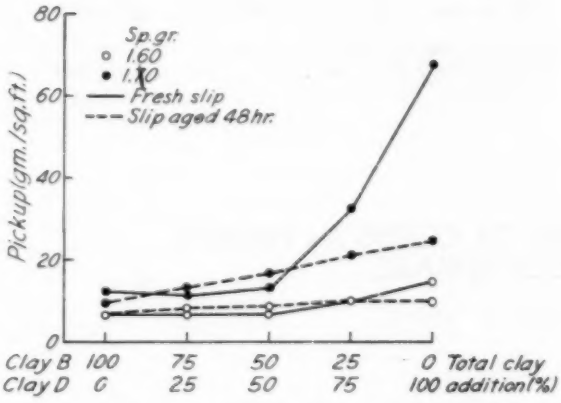

FIG. 15.—Pickup vs. clay blend for ground-coat slip and clays B and D.

They were then dried and weighed to determine the amount of enamel retained.

In some preliminary work, there was a noticeable leveling of the pickup values at low specific gravities and also some change in the value, depending on the age of the enamel slip. In order to cover a range of conditions, tests were made at specific gravities of 1.65 and 1.75, both when the slips were fresh and after they had been aged for 48 hours. The results of these tests are shown in Figs. 6, 7, 8, 9, 10, and 11. A noticeable decrease in pickup was observed after aging. This effect was less pronounced with the low-set clays than with those having the higher initial pickup values. The leveling off of the pickup values at the lower specific gravities is also apparent. In general, the pickup weight increased from clays A or B to clay E, irrespective of the type of frit used, and this trend, therefore, may be controlled to some extent by the initial salt content of the clays. The rate of increase, however, varied considerably with the different compositions.

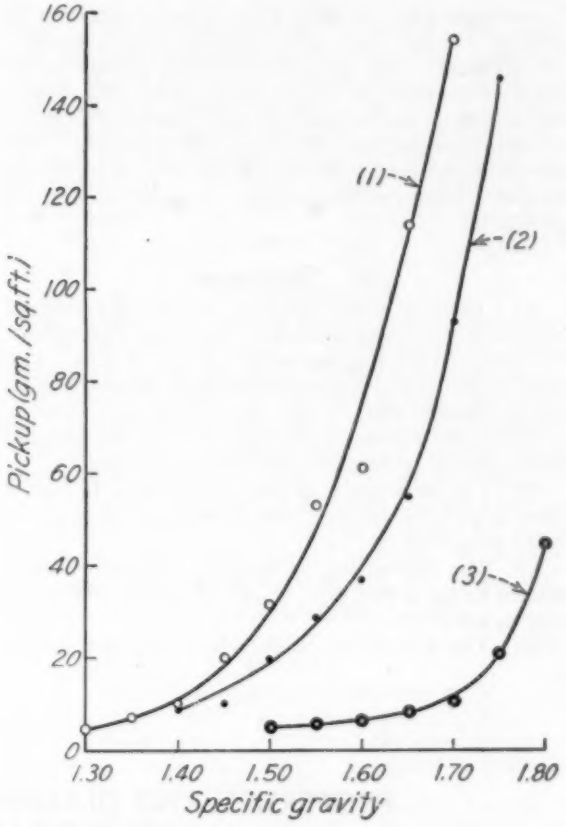

FIG. 16.—Pickup vs. specific gravity for various frit and clay combinations; *curve (1)*, frit E and clay A with $BaCl_2$ added; *curve (2)*, frit D and clay E; and *curve (3)*, frit E and clay A.

(2) Clay Combinations

Many cases exist in practice where it is desirable to use a combination of clays. In order to study the effect of using different clay combinations, millings were made with high- and low-set clays in various proportions. Frit D and a blend containing frits A, B, and C were used in these tests. The results are given in Figs. 12, 13, 14, and 15. It is to be noted that in all combinations tried, the pickup weight obtained with a mixture containing equal proportions of two clays was never the average of the two clays alone. Instead, this weight was generally nearer that for the lower set clay than for the higher. The mill additions used in these tests were as follows:

Frit	Fig. 12 Parts	Fig. 13 Parts
A		250
B		250
C		500
D	1000	
Clay	80	70
Water	425	450

A similar relationship exists between the pickup weight and the specific gravity of the enamel slip, as is shown

by comparing the curves in Figs. 12 to 15 with those in Fig. 16. If any two points are taken on a specific-gravity curve, the intermediate points will always be less than the average of the original points. The variation in pickup thus is similar either when blending clays or when changing the specific gravity of the slip. The marked tendency for pickup values to level off in the ranges of lower specific gravities can again be observed in Fig. 16.

V. Conclusions

(1) There is some variation in the mineralogical composition of these enameling clays which are known to have good working properties in enamel slips. The chief variation is in the quartz and illite content. There was no decided effect of this variation on the properties of the enamel slips used, although the clays showing the lowest pickup probably contained the most quartz.

(2) For these clays, it was not possible to find a direct correlation between their particle size and various other properties.

(3) The pickup on the samples studied is closely related to the initial salt content as shown by the hydrogen-ion curves.

(4) The weight loss of the clays does not appear to be related to the bubble structure in the fired enamels, although some correlation might be expected.

(5) For all the clays examined, the amount of bubbles in the fired enamels is roughly proportional to the total carbon content of the raw clay as determined by combustion methods.

(6) The pickup of enamel slip varies considerably with the type of clay used.

(7) The pickup of the slip varies with the type of frit used.

(8) The pickup obtained with a mixture of two clays is usually less than the average of the values for the two clays alone.

(9) The pickup weight increases more and more rapidly as the specific gravity is raised with the result that, if slips of different specific gravities are mixed, the slip produced will have a lower pickup than the average of the initial values for the two slips.

Acknowledgment

The authors wish to express their indebtedness to A. O. Tesar for his assistance in making some of the tests and to G. Bumblis for running the carbon determinations.

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PROPERTIES AND DIAGNOSIS OF CORDS IN PRESSED AND BLOWN GLASSWARE*

BY L. G. GHERING AND M. A. KNIGHT

ABSTRACT

Cords are characterized by more or less abrupt changes in physical and chemical properties in localized areas of the glass. The available methods for determining the properties and practical aspects of cords that occur in pressed and blown glassware are described. The properties of cords are considered in relation to the determination of their sources and causes. The manner in which cords affect the physical properties of glassware and the procedures for evaluating these effects are discussed.

I. Introduction

This paper is a general discussion of the properties and the practical aspects of cords that occur in pressed and blown glassware; it is primarily intended for the plant operator. It is hoped that it will also prove of general value as an outline of the available information on cords. The large variety of methods that have been used in the glass industry for detecting and evaluating cords are reviewed; these are amplified and extended through data accumulated in the cord research program in this laboratory. Typical data will be presented to demonstrate various types of information that a laboratory can obtain in the study of cords.

The word cord brings somewhat differing pictures to various people in the glass plant. Four of such general points of view are outlined below:

(1) The workmen on the "hot end" think of cords as lumps or streaks of glass of high viscosity that tend to form ridges in the ware. These local areas of the gob do not work in the same way as the remainder of the glass; they do not blow out evenly. For example, a piece of ware may have a narrow ridge of glass along one side in spite of attempts to change mold temperatures or other forming details.

(2) To the packing room, cords are appearance defects in the finished ware. These may be thick streaks or ridges through the wall. They may be very narrow filaments or threads leaving tiny ridges or grooves on the surface, sometimes referred to as "cat scratches" in bottle plants, or they may be noticeable differences in refractive index.

* Taken in part from paper presented under the title "Cords," by L. G. Ghering at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (Glass Division). Received June 29, 1944.

(3) To the laboratory, cords are portions of the glass that show unusual polariscopic strain associated with fairly sharp boundaries. Differences in refractive index, color, density, etc., also are present.

(4) In the optical glass industry, differences in the optical properties, especially refractive index, are all important. This point of view will be omitted in the present discussion.

All of these ideas of cords are based on the presence of differences in physical properties between adjacent parts of the glass. Cords can be defined as streaks, laminations, or local irregularities in the glass that differ from the bulk, or matrix glass, in their physical properties (primarily those of density, refractive index, and coefficient of thermal expansion) and in their chemical compositions. Ridges and grooves that are formed "mechanically" in glass of uniform composition, but which to casual inspection sometimes have the same appearance as certain types of cords, are excluded by this definition.

II. Thermal History

In the technical literature,[1] there is ample evidence that the thermal history of glasses influences their physical properties of thermal expansion, density, refractive index, etc. For example, it is well known that at room temperature the density of a glass of a given composition depends on its temperature history in the annealing range. Approximate figures for the relation between density* and rate of cooling are given in Table I for a representative bottle glass composition.† This difference in density, of course, is due to the fact that the ionic spacing "frozen" into the glass depends on the rate of cooling. Very rapid cooling, such as quenching, freezes into the glass a "wide" ionic spacing characteristic of a high temperature. Such glass is therefore less dense than that cooled very slowly in the annealing range. The same sort of thing is true for the other physical properties. The important temperature effects, however, occur only in the annealing range. At furnace temperatures, it does not take long for glass to reach an equilibrium state and differences in properties are insignificant.

Commercial annealing subjects all adjacent areas in the ware to very nearly the same heat-treatment, and it does not cause local irregularities. Even the extreme temperature differences produced in the forming process do not cause cords. Glassware, as it is formed in the mold, has a cooled skin on the surface next to the mold; this is often referred to as an "enamel skin." The interior glass is hot; in fact, the skin of a molded container is probably at a temperature of 700° to 1000°F. while the interior may be 1200° to 1600°F. These are large temperature differences, and the lower temperature is below the upper annealing range. In other words, the temperature history of the interior and the outside of every blown piece of ware is quite different. No one, however, claims that a cord is produced by this difference in temperature history. Other physical and chemical differences must already be present if there is to be cord in the ware.

III. Cold-Glass Cords

The workman on the hot end recognizes that some of the viscous cords have a high-alumina or silica content; it is well known that an increase in either or both of these could account for the high viscosity; however, he also refers to some cords as "cold cords" or "thermal cords." Knowing that lower temperatures increase viscosity, he postulates that cold glass of high viscosity is being drawn in with the normal glass of the same composition and that he is trying to make ware out of two samples having viscosities that differ because of temperature differences alone. This does not appear to be a true picture of the problem.

TABLE I

EFFECT OF ANNEALING ON DENSITY

Heat-treatment	Density (gm./cc.)	Increase (gm./cc.)
Unannealed, "set out" bottle	2.500	0.000
High-strain, commercial, temper No. 4*	2.505	0.005
Low-strain, commercial, temper No. 1*	2.507	0.007
3.2°F./hr. cooling rate	2.512	0.012

* For explanation of temper gradings, see Standard Method of Polariscopic Examination of Glass Containers, A.S.T.M. Designation C 148–43.

It has been pointed out[2] that ridges or waves may be formed when two samples of a glass at different temperatures are brought together in such a way that there is not sufficient time for temperature equilibrium to be attained prior to or during the fabrication process. Two samples of a glass at different temperatures that are brought together above 1800°F. will rapidly reach the same temperature and the same equilibrium, molecularly speaking, and hence the same viscosity. When a difference in viscosity persists, it is almost certain to do so for some reason other than a temperature difference. Such "viscosity" ridges or waves are freaks that are not common in the normal processes; they should not be called cords unless a difference in density, refractive index, thermal expansion, etc., is also present. All so-called temperature or cold-glass cords are probably composition cords. There is opportunity for composition differences to exist as follows: The batch may be off composition or may not be completely mixed; there may be segregation in the melt with formation of silica scum; refractory contamination

[1] G. W. Morey, Properties of Glass, pp. 141, 244, 267, and 383. Amer. Chem. Soc., Monograph Series, Reinhold Publishing Corp., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48 (1939).

* All density values in this paper are given in grams per cubic centimeter.

† Unpublished memorandum of the Standard Testing Procedure Committee of the Glass Container Association compiled from Preston Laboratories data and private communications from the Owens-Illinois General Research Laboratory, Hartford-Empire Company, and Armstrong Cork Company.

[2] "Additional Letters Establish Source of Cords," *Ceram. Ind.*, **41** [No. 6, December] 53–55 (1943); *Ceram. Abs.*, **23** [6] 102 (1944).

may occur, etc. All data obtained to date in this laboratory verify this picture; so-called cold-glass cords show definite composition differences from the matrix glasses.

IV. Composition and Thermal Expansion

Cords are not apt to be noticed on the hot end unless the composition changes are such that the viscosity differences between the cord and matrix glasses are relatively high. Usually, the other physical properties also are changed considerably. The composition, however, may vary in such a way that the viscosity difference is relatively small and the expansion difference relatively large. Such cords are recognized only by the use of the polariscope; the difference in expansion produces strain which is visible in polarized light.

If the composition difference is known, the difference in expansion and hence in relative amount of polariscopic strain may be calculated approximately from the set of factors* given in Table II; these factors apply only to typical soda-lime-silica bottle glasses. Each factor gives the change in the glass expansion coefficient that is caused by an increase of 1%† in the respective oxide.

TABLE II

FACTORS FOR CALCULATING COEFFICIENT OF THERMAL EXPANSION OF SODA-LIME-SILICA GLASSES

Oxide	Factor (in./in./°C.) per %	Oxide	Factor (in./in./°C.) per %
Na_2O	3.86×10^{-7}	Li_2O	6.56×10^{-7}
K_2O	3.20×10^{-7}	BaO	1.08×10^{-7}
CaO	1.36×10^{-7}	SiO_2	0.28×10^{-7}
CaO·MgO	1.10×10^{-7}	Al_2O_3	0.24×10^{-7}
MgO	0.73×10^{-7}	B_2O_3	-0.60×10^{-7}

Note that soda has a high factor, lime is intermediate, while alumina and silica give lower expansions. Boron, the important ingredient of borosilicate, low-expansion glasses, is unusual in that, in small amounts only, it has a negative factor; that is, the addition of boron decreases the expansion. From Table II, it is seen that replacing 1% of silica by soda (soda, +1%; silica, −1%) increases the expansion 3.58×10^{-7} in. per in. per °C. The method of calculation is as follows:

For soda, $+1.0 \times 3.86 \times 10^{-7} = 3.86 \times 10^{-7}$
For silica, $-1.0 \times 0.28 \times 10^{-7} = -0.28 \times 10^{-7}$
Total change $= 3.58 \times 10^{-7}$

It is not possible to predict the composition change accurately just from the stress measurements in the polariscope. However, oxides with high-expansion coefficients lead to tension cords, whereas low coefficients are associated with compression cords. A high coefficient of expansion in a cord causes a large shrinkage of the glass after it has set in the softening range of temperature; this leads in the cooled ware to a tension cord (one in tension along its length). Such a cord is probably due to high soda and low lime, low silica, or low alumina; it cannot come from refractory corrosion. Conversely, a compression cord, being caused by oxides with low-expansion coefficients, is very likely high in silica or alumina or both and probably comes from refractories or from silica scum. A better prediction as to the composition difference can be made if the change in some second physical property, such as density, is also known. Such interpretations are discussed further in section IX.

V. Composition and Density—Density Calculations

The calculation of density from composition by the use of factors is well known.[3] A set of such factors[3(c)] is given in Table III. The factor for boron applies only to glasses containing less than 80% of SiO_2 and less than 8% of B_2O_3.

TABLE III

HUGGINS' FACTORS FOR CALCULATING DENSITY

Component oxide (M_mO_n)	d_M	$Z_M(N_{Si} = 0.345–0.400)$	$Z_M(N_{Si} = 0.400–0.435)$	$Z_M(N_{Si} = 0.435–0.500)$
SiO_2	2.00	2.34	2.27	2.20
Na_2O	0.97	2.87	3.09	3.56
K_2O	0.64	2.68	2.79	3.04
CaO	1.07	3.87	4.31	5.44
MgO	1.49	2.78	3.10	3.91
BaO	0.39	7.6	8.2	9.6
Al_2O_3	1.77	2.4	2.7	3.4
B_2O_3	2.59	1.9	2.2	2.9
PbO	0.27	10	11	12
ZnO	0.74	5.4	5.9	7.4

The density, ρ, in gm./cc. at 20°C., is found by equation (1).

$$1/\rho = f_1/Z_1 + f_2/Z_2 + f_3/Z_3 + \ldots \quad (1)$$

f_M = fractional amount of oxide of M.
Z_M = factor given in Table III.

In order to find the appropriate set of factors, calculate N_{Si} by equation (2).

$$N_{Si} = f_{Si}/(d_1f_1 + d_2f_2 + d_3f_3 + \ldots \quad (2)$$

d_M = values given in Table III.

By inspection of these factors, the direction and the relative amount of change in density caused by the addition of any particular oxide to a base glass (dilution) can be determined. From the composition of the base glass, the proper Z_M column is found by use of the N_{Si} formula at the bottom of the table. The addition of any oxide that has a factor greater than the density of the base glass increases that density; oxides with factors less than the density of the base glass decrease the density. These effects are in proportion to the differences between the density of the base glass and the factors for the respective oxides. For example, consider a glass with approximately 70% silica and a density of 2.50; the middle Z_M column applies here. Be-

* Courtesy of Owens-Illinois Glass Company General Research Laboratory, Toledo, Ohio.

† Unless otherwise indicated, all compositions are given as per cent by weight.

[3] (*a*) M. L. Huggins, "Silicate Glasses, Calculation of Density," *Ind. Eng. Chem.*, **32** [11] 1433–36 (1940); *Ceram. Abs.*, **20** [2] 42 (1941).
(*b*) "Calculation of Density," *Glass Ind.*, **22** [5] 228–29 (1941); *Ceram. Abs.*, **20** [8] 191 (1941).
(*c*) M. L. Huggins and K.-H. Sun, "Calculation of Density and Optical Constants of Glass from Its Composition in Weight Percentage," *Jour. Amer. Ceram. Soc.*, **26** [1] 4–11 (1943).
(*d*) "Calculation of Density," *Glass Ind.*, **24** [7] 298, 310 (1943); *Ceram. Abs.*, **22** [10] 169 (1943).

cause of its factor of 2.27, silica decreases the density slightly. Alumina increases it somewhat, while soda gives a greater increase. Calcium oxide, with a factor of 4.31, causes a still greater change.

The factors in Table III are not in the most convenient form for calculation of the approximate density differences caused by small composition differences such as are very often found in cordy glasses. For this purpose, a more useful set of factors can be calculated from those given by Huggins.[3] Equation (1) for computing density may be differentiated to yield equation (3).

$$-\frac{1}{\rho^2}d\rho = \frac{df_1}{Z_1} + \frac{df_2}{Z_2} + \frac{df_3}{Z_3} + \ldots \qquad (3)$$

Equation (3) is exact only for extremely small changes; when only small changes are involved, increments can be substituted for the differentials and an approximate equation can be obtained. With weight percentage, x_M, substituted for weight fractions, f_M, this becomes equation (4).

$$\Delta\rho = -0.01\rho^2\left(\frac{\Delta x_1}{Z_1} + \frac{\Delta x_2}{Z_2} + \frac{\Delta x_3}{Z_3} + \ldots\right) \qquad (4)$$

Equation (4) holds with sufficient accuracy up to Δx_M changes of about 3% for the component showing the greatest change. When a new factor, Y_M, defined by equation (5), is substituted in equation (4), equation (6) is found.

$$Y_M = \frac{-0.01\ \rho^2}{Z_M} \qquad (5)$$

$$\Delta\rho = Y_1\Delta x_1 + Y_2\Delta x_2 + Y_3\Delta x_3 + \ldots \qquad (6)$$

Table IV gives values of Y_M for a glass having ρ = 2.49 and with a silica content between 69 and 75%. These values hold for a range of glasses, as discussed below.

TABLE IV

FACTORS FOR CALCULATION OF DENSITY DIFFERENCES*

Oxide	Y_M (gm./cc./%)	Oxide	Y_M (gm./cc./%)
SiO_2	−0.0273	Na_2O	−0.0200
Al_2O_3	−0.0232	K_2O	−0.0222
CaO	−0.0143	B_2O_3	−0.0281
CaO·MgO	−0.0163	ZnO	−0.0105
MgO	−0.0199	PbO	−0.0056
BaO	−0.0075		

* These factors apply to bottle glasses of approximately 2.49 gm. per cc. density containing between 69 and 75% silica.

The factors Y_M can be used for computing density differences with a maximum error in the difference of approximately ±0.0005 when the base matrix glass density is in the range of 2.43 to 2.55 and when the change in composition is not greater than 1%. If the density is limited to the range of 2.45 to 2.53, differences up to 2% in the major composition change give maximum errors of ±0.0005 in the density difference. For densities outside the 2.43 to 2.55 range, the matrix glass density can be substituted in equation (4) to yield a new set of factors similar to those in Table IV or the complete computations of the densities of both matrix and cord glasses can be made by equation (1), giving the difference directly. When the composition differences are greater than 3%, the latter method must be used.

In all calculations involving the factors Z_M, it is important to use the proper Z factor from Table III as determined by the value of N_{Si} (equation (2)).

VI. Density Measurement Methods

(1) Archimedes' Principle

The older method of determining the density or specific gravity of glass by means of Archimedes' principle[4] (weighing in air and in water in a platinum wire basket) is useful for determining the representative density of large lumps of glass. It is not well suited, however, to the determination of the density of a cord. Usually only a small chip or lump representative of the cord is available here, and a comparison with the matrix glass is of more interest than absolute values.

(2) Sink-Float: Composition of Liquid Varied

For testing cords, a sink-float method is useful. In one of these methods,[5] the small chip of glass is floated in a mixture of heavy and light liquids, with the ratio of the liquids being adjusted until the mixture matches the density of the sample. The density of the liquid is then determined by means of a standard lump of glass.

(3) Sink-Float: Temperature of Liquid Varied

In another technique, the density of the liquid mixture is adjusted to that of the sample by control of their temperature. A standard density sample of approximately the same density as the unknown is put in the tube with the unknown, and the temperatures at which the two respective samples match the liquid are then determined. The density of the unknown is calculated from the predetermined temperature coefficients of density for the liquid and the glass. Measurements of this type for plant-operating purposes can be made with a thermometer, test tube, and water bath on lumps approximating a 1/4-in. cube.

(4) Sink-Float Centrifuge Method

With small lumps and especially with powders from 20- to 200-mesh, a centrifuge[6] is necessary to increase the effect of gravity and thereby to cause more rapid settling of the glass. The centrifuge also allows greater accuracy in the measurements and permits the use of the pressure gradient[6(b)] in the tube for determining

[4] "Glass Composition Control by Use of Specific-Gravity Determinations," *Glass Ind.*, **22** [9] 384–86 (1941); *Ceram. Abs.*, **21** [1] 8 (1942).

[5] T. C. Vaughan, "Determination of Density by Flotation Method," *Bull. Amer. Ceram. Soc.*, **23** [2] 68–69 (1944).

[6] (*a*) J. C. Turnbull, "Separation of Inhomogeneities in Bottle Glass by Density Differences," *Jour. Amer. Ceram. Soc.*, **24** [2] 37–43 (1941).

(*b*) J. C. Turnbull and L. G. Ghering, "Cord Analysis," *ibid.*, **24** [8] 264–70 (1941).

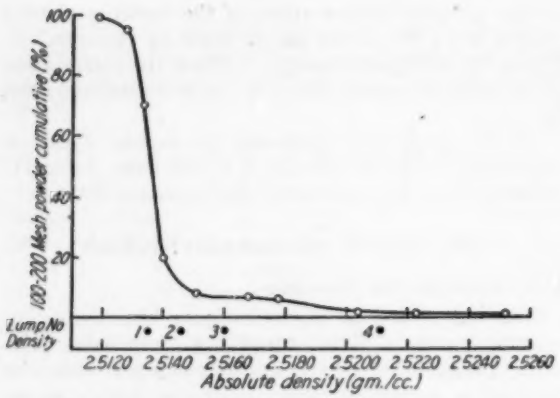

FIG. 1.—Density distribution curve of representative glass and lump densities of selected pieces from 12-oz. bottle showing a localized, high-density cord. Lump No. 1, 180 degrees from cordy streak; No. 2, 90 degrees from cordy streak; No. 3, full thickness of wall in cordy streak; and No. 4, thin piece of cord from outside surface of wall (inside surface, noncordy glass ground away).

relative densities of lumps or powder particles with a precision of about ±0.00002 gm. per cc. When powder is used in the centrifuge, it is possible to run a density-distribution curve[6(b),7] of the powder.* Separations of various fractions of the powdered sample can be made on the basis of their density differences; these fractions are useful for chemical analyses and other tests.

The liquids currently used by the present authors in this flotation work are α-bromonaphthalene and *s*-tetrabromoethane; mixtures of these liquids are prepared moisture-free under reflux in vacuum at 100°C. The effective factor for the change of density with temperature is 0.00171 gm. per cc. per °C. for mixtures having densities in the range of 2.4 to 2.6. This factor is to be applied directly to the glass samples since it takes into account the temperature coefficient of density for bottle glasses having coefficients of cubical expansion between 2.6 and 3.2×10^{-5} cc. per cc. per °C. and densities about 2.5 gm. per cc.

The kinds of density data obtainable with the centrifuge are illustrated by Fig. 1. The samples under test were taken from the shoulder of a bottle showing a high-density cord that was well localized along one side of the bottle. The results show the relationship between lump densities from selected areas and the density-distribution curve of representative glass. The heavy glass from the cord appears in the high-density tail on the curve and in lump No. 4.

VII. Separation of Cords from Matrix

If regions of the glass that differ as to their properties can be separated mechanically, then chemical analyses and other tests can be made directly on the separated fractions. If the chemical analyses are done accurately, they give a definite answer as to what composition differences are involved in the cord. In certain cases, pieces of the cordy glass can be chipped or melted away from the rest of the glass.[8] Semimicrochemical determinations can be applied to these products.

Separations on the basis of density differences can be made on powdered samples in the centrifuge.[6(b)] Chemical analyses can then be made on samples of any desired density range. The size of the fraction obtained is regulated by the nature of the cord and by the tests that are desired and can be varied at will. With fine cords, for example, the cat-scratch surface cords, the amount of cord is so small that usually only small samples are obtained for analysis. Nevertheless, quite satisfactory methods of analysis have been developed for these small samples.

The authors have cooperated with other laboratories to a limited extent in spectroscopic analysis of certain samples. This has proved to be especially useful when refractory or metallic contamination is suspected. It is feasible here to trace the contamination through data on unusual or minor ingredients, such as iron, zirconium, vanadium, tin, lead, etc. Further work needs to be done on the application of spectroscopic methods to glass analysis.

VIII. Cords and Mechanical Strength

(1) Pertinent Stresses

It is well known that some cords are detrimental to the mechanical strength of ware while others are not. The reason for this is fairly simple. Glassware breaks only because of tension stresses at a surface. Fractures always originate on a surface, and whenever the tension stress at a surface reaches a value of about 4000 to 6000 lb. per sq. in.* on commercial glassware, a fracture may start. The tension stress may be applied stress, such as that caused by loading a glass beam, dropping glassware on to the floor, putting pressure inside a bottle, or subjecting glass to an unusual temperature change; all of these produce tension on some surface. There may also be another type of tensile stress in the ware, namely, permanent stress put into the ware at the time it is made. Annealing stress and cord stress are the important permanent stresses. It is worth emphasizing

[7] (*a*) F. V. Tooley and R. L. Tiede, "Factors Affecting Degree of Homogeneity of Glass," *Jour. Amer. Ceram. Soc.*, **27** [2] 42–45 (1944).

(*b*) R. L. Tiede and F. V. Tooley, "Effect of Temperature on Homogenizing Rate of Soda-Lime-Silica Glass." Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5,1944 (Glass Division); to be published in an early issue of this *Journal*.

* Note that Tooley and Tiede plot the curves with the cumulative per cent of glass at the top of the tube as ordinates and with increasing temperature of the liquid as abscissas, while Turnbull and Ghering in their early work[6] plot cumulative curves for the per cent of powder on the bottom of the tube versus increasing temperature. The present authors plot per cent of powder below the 20-mm. level in the tube versus the increasing (absolute) density (decreasing temperature) at that level; this gives a curve of the same form as those by Tooley and Tiede.

[8] G. J. Zarbo, H. J. Hunt, and D. C. Smith, "Analysis of Cords and Stones," *Jour. Amer. Ceram. Soc.*, **27** [5] 138–42 (1944).

* All stress values are expressed in pounds per square inch.

here that stresses from cords cannot be removed by annealing because the stress arises from a difference in coefficient of thermal expansion between the matrix and the cord. This difference in coefficient is due primarily to a composition difference, and it cannot be eliminated through annealing.

When these stresses are considered, the location of tension stresses with respect to the surface of the ware becomes the all-important matter. A tension cord with a permanent tension stress of 2500 completely buried within a wall will not cause breakage. However, the same cord on a surface may produce an appreciable surface crack. If the ultimate breaking tension of the ware is 4000 to 6000, the permanent stress of 2500 reduces the effective strength by about one half. Measurements of cord stresses in various locations in the wall have confirmed this picture of cord breakage beyond all doubt. Study of many bottles where a cord with tension of 2000, or more, outcropped on the surface has shown that fractures always begin in the area of outcropping tension.

Compression stresses are ignored whether arising from cord or annealing, since glass breaks only under tension. In the case of cords, it is not the location of the cord that matters so much as the location of any tension stresses associated with it. For example, if a compression cord lies near a surface, it may induce tension stress at the surface; in this case, the induced tension is the important thing.

(2) Evaluation of Cord Stresses in Ware

It is seen, then, that the most important consideration in grading cords in the polariscope is to determine the location of the cord with respect to the surfaces of the ware and the amount of tensile stress in the cord or induced in the glass adjacent to the cord. In machine-blown ware, the cord or cords may be in the concentric layers. Since the polariscope is a two-dimensional tool, looking through the wall of a piece of ware, such as a tumbler or bottle, perpendicular to its axis is like looking perpendicularly at the layers of an onion. In order to see the layers, it is necessary to look at them edgewise. Similarly, in the examinations of cordy ware, it is informative to look at the ware edgewise, as in a ring section.

A recent publication[9] describes in detail a method of measuring tension stresses in ware by means of the polarizing microscope and of grading the ware from the point of view of mechanical strength. The tension stresses are weighted according to their locations in the ware. Cord stresses, both direct and induced, and annealing stresses are treated alike. Since a tension in the interior has much less effect on mechanical strength than has one on the surface, the highest tension stress in the interior is multiplied by one third in order that such stresses will have less weight. The highest tension stress on the inside surface is multiplied by two thirds and that on the outside surface is multiplied by one. The largest of these resulting values is called the stress index of the ware. A tension of 1800 thus produces a stress index of 600 if it is in the interior, 1200 if it outcrops on the inside surface, and 1800 if it outcrops on the outside surface.

From the foregoing discussion, it is seen that the polariscope or a direct mechanical strength test is essential in the evaluation of the mechanical strength of ware. A density-distribution curve gives valuable information concerning the homogeneity of the glass; it gives a basis for grading the glass quality. Chemical analyses on separated fractions give additional information. Such techniques, however, do not give specific information on the mechanical strength of fabricated ware; they give neither the amount nor the location of the tensile stresses. With respect to the effect of cords on mechanical strength, any method of judging the ware solely on the basis of the presence or absence of lumpy ridges or streaks may be misleading. Most lumpy cords are compression cords rich in silica and alumina, and the effect of such cords on mechanical strength depends on the amount of induced tension, if any, on the surface of the ware. In the modern gob process for blown bottles, the most troublesome cords from the point of view of mechanical strength usually are concentric tension cords on the outside surface. These are high in lime and soda and frequently show no lumpiness whatsoever.

IX. Interpretation of Stress and Density Data

If both the stress produced by a cord and the density difference of the cord as compared with the matrix glass are known for a given geometric configuration of the cord, it is possible to estimate the probable composition difference. For example, if the cord is a high tensile stress cord (1500) with a high density increase (0.0100), it is most likely to be rich in soda or lime, or both, and low in silica (about 1.0%). A higher stress (2000) with the same difference in density would indicate a higher soda-to-lime ratio in the cord since soda increases expansion (and hence stress) faster than lime. Conversely, a lower stress (1000) with the same density difference indicates a lower soda-to-lime ratio. Similarly, if a cord is one with compression stress, it is probably rich in silica or alumina or both since these are the low-expansion components. In the case of cords rich in both alumina and silica, however, it is possible to have a zero density change because alumina and silica in certain proportions exactly compensate each other with respect to density.

It is difficult to make estimates of this sort unless some experience and data have been accumulated on composition differences, density differences, and stress on previous cords in a given composition. With this information, comparisons are easier and predictions as to which components are producing the observed density changes and stresses are more apt to be accurate. Such predictions, furthermore, are more practicable when there are other clues as to the cause and origin of the cord. Usually the plant man does have other clues; he can confirm or disprove these by predicting composition difference from density difference and stress data.

[9] Glass Container Association of America, "Polariscopic Examination of Glass Container Sections," *Jour. Amer. Ceram. Soc.*, **27** [3] 85–89 (1944).

In the final analysis, however, the best answer to the question of composition change comes from careful separation of the cord and accurate chemical analyses of the fractions. The best method for the separation of cords appears to be the centrifuge technique based on density differences.

X. Summary

The diagnosis of cords in glass is a complex problem which must be approached in a variety of ways. All available operating data have to be considered; batch composition and mixing must be checked, furnace operation must be studied, and any evidence of refractory corrosion must be investigated. Results of laboratory tests must also be correlated with the plant data.

Informative properties that aid in the detection and evaluation of cords include (1) viscosity differences in the glass apparent on the hot end, (2) lumpiness, ridges, or grooves in the finished ware, (3) refractive index differences visible to the naked eye, (4) density differences measured in the laboratory and calculated from composition data, (5) unusual strain seen in the polariscope, especially when a wall section is viewed edgewise, and (6) composition differences between separated fractions of the glass.

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TIME PROBLEM IN ANNEALING*

By Aniuta Winter

Abstract

A discussion of the homogeneity and stability that can be obtained by submitting a sample of glass to a given cooling schedule leads to a new method of annealing called the "freezing process." The problems (*a*) how to obtain a given degree of annealing in a minimum amount of time and (*b*) how to obtain the best possible annealing in a given time are discussed theoretically in conjunction with the general principles of glass annealing. Numerical values of different quantities involved are given, and the application of the freezing process to a light flint glass is described in detail.

I. Introduction

A description of the behavior of glass during changes of temperature has been given in a previous paper.[1] A method was established for determining annealing schedules that in a minimum of time will give the best-annealed glass, that is, the "limit annealing" defined herein.* The present paper is concerned with the different problems that arise when the best possible annealing is not needed. The importance of structural homogeneity in various uses of glass is emphasized, and the whole problem of annealing is considered primarily as a means of attaining this homogeneity.

The importance of the structural homogeneity and the manner in which its absence affects the glass in practical use have been described in a previous paper.[2] Structural heterogeneity means a variation of physical constants of glass from one point to another with the chemical composition of the glass the same throughout its volume.

In the present paper, the chemical composition will be assumed to remain the same for the whole mass of glass under consideration and the previously given definition of structural homogeneity will be maintained. As far as thermal treatment is concerned, such homogeneity may be obtained by proper annealing and heterogeneity may be introduced again by different cooling schedules.

II. Formulation of the Problem

The problem of glass annealing is one of physicochemical equilibrium. When glass has had optimum annealing, it is in equilibrium at the temperature at which it is used; such glass may be said to be stabilized because it does not vary with time. Such glass is necessarily structurally homogeneous. The thermal treatment by which these optimum results are obtained may be called the "limit annealing."

For practical purposes, however, this limit is seldom needed. Even for many precision uses, a less stabilized glass can be utilized if it is homogeneous and if its aging is sufficiently slow. The problem to be discussed here is (*a*) whether it is possible to obtain a glass homogeneous enough for a given purpose without its having been completely stabilized and (*b*) how maximum gain of time can be obtained for a given degree of homogeneity by accepting a given tolerance of stability; in other words, how to obtain a given degree of annealing in the shortest time or the best possible annealing in a given time.

III. Theoretical Considerations

The answer to this problem must be sought in the behavior of glass during changes in temperature. Some of the results published in previous papers will

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Glass Division). Received April 3, 1944; revised paper received June 15, 1944.

[1] Aniuta Winter, "Transformation Region of Glass," *Jour. Amer. Ceram. Soc.*, **26** [6] 189–200 (1943).

[*] *Ibid.*, p. 196.

[2] Aniuta Winter, "Structural Homogeneity of Glass," *ibid.*, **26** [8] 277–84 (1943).

therefore be reviewed.[1,2] For each temperature at which glass is maintained, there is a corresponding state of equilibrium, which generally is reached simultaneously with the thermal equilibrium. There is, however, a temperature interval called the transformation region[1] in which structural equilibrium does not follow the thermal equilibrium instantaneously, that is, after the temperature has been changed and thermal equilibrium attained, the glass must be maintained at the new temperature for a definite time before reaching structural equilibrium.

For a given change in temperature, the transformation time that elapses between the thermal and structural equilibrium decreases as the temperature of equilibrium increases, that is, the average speed of transformation increases with temperature.

The actual instantaneous speed of transformation for an isothermal operation, however, is not constant; it decreases exponentially from its maximum value at the start and tends asymptotically toward zero as the time increases. These results can be represented quantitatively by choosing some physical constant that will characterize the state of glass. The refractive index will be used as the characteristic constant in the following considerations.

The variation of refractive index from the time, $t = 0$, when the thermal equilibrium is attained and as long as the temperature, T, remains constant, is represented by the empirical law[3] given in equation (1).

$$n = n_T + (n_0 - n_T)e^{-Bt} \qquad (1)$$

n = refractive index at time t.
n_0 = refractive index at time 0.
n_T = refractive index of equilibrium at temperature, T (i.e., the value to which n tends when $t \to \infty$).
B = a parameter independent of time but a function of temperature.

The instantaneous speed of transformation at constant temperature of equilibrium, T, is therefore given by equation (2).

$$v_T = \frac{dn}{dt} = -B(n_0 - n_T)e^{-Bt} \qquad (2)$$

Equations (1) and (2) call for the following remarks:

(*A*) Equation (1) shows that the glass tends asymptotically toward the state of equilibrium when t tends toward infinity. It must be specified, therefore, what is understood in practice by the term "reaching equilibrium." In the following discussion, this phrase will mean that the difference $(n - n_T)$* is negligible for the purpose for which the glass is to be used.

(*B*) In the transformation region for most glasses, n_T has been found to increase as T decreases; outside this region, n_T increases with temperature.

(*C*) Equation (2) shows that the initial speed of transformation (given in equation (3)),

$$v_i = B(n_T - n_0) \qquad (3)$$

depends on two factors, namely, the difference $(n_T - n_0)$ and the parameter, B.

For most glasses, when n_0 = a constant (the same initial state of equilibrium), the difference $(n_T - n_0)$ decreases when the temperature increases within the transformation region and it increases outside this region. Except in the vicinity of the limit of the transformation region, the variation of $(n_T - n_0)$ seems to be an almost linear function of temperature. The parameter, B, remains constant during an isothermal operation and varies only with the temperature.

Figure 8 shows B as a function of temperature for a light flint glass. The numerical values for B may be different from one glass to another, but the general trend of this curve, $B = f(T)$, seems to remain the same. This figure shows (*a*) that B increases with temperature and (*b*) that the variation of B below the transformation region and in the lower part of this region is relatively slow; in the upper part of the transformation region, B varies rapidly. The variation of the transformation speed with the temperature shows the same general trend as B. The faster the variation of B, moreover, the more rapid will be the variation in the speed of transformation. The glasses in which B varies more rapidly will therefore require a more precise annealing temperature, which makes the annealing operation more delicate.

It is obvious that when a glass is cooled from temperature T_1 to a temperature, T_2, the time necessary to reach equilibrium corresponding to T_2 depends on the speed of cooling; equation (3) suggests the existence of an optimum variation of temperature with time† because the factors B and $(n_T - n_0)$ vary with the temperature in opposite directions.

If the variation of temperature is too slow, the speed of transformation will be low because of the small value of $(n_T - n_0)$. If the variation of temperature is too fast, the speed of transformation will be low because B diminishes rapidly with he temperature. These conclusions have been confirmed by exact calculations.

IV. Factors Determining the Annealing Schedule

The extremely rapid decrease of the speed of transformation with temperature and its low value in the vicinity of the lower limit of the transformation region, T_a,‡ make the entire problem of annealing one

[3] For equation (1), see p. 193 of footnote 1; two other equations have since been proposed for this phenomenon as follows: (*a*) N. W. Taylor and Bradford Noyes, Jr., "Aging of Thermometers," *Jour. Amer. Ceram. Soc.*, **27** [2] 57–62 (1944); p. 59; (*b*) Harold McMaster proposes an equation of secondary reactions for this phenomenon in "Variations of Refractive Index of Glass with Time and Temperature in Annealing Region." Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 to be published later in this *Journal*.

* For precision uses in optics, it is assumed that $n - n_T = 1 \times 10^{-5}$; for many other uses, when the problem of refraction is unimportant, the value $n - n_T = 1 \times 10^{-3}$, may guarantee enough stability; no greater precision than 1×10^{-5} can be required unless special precautions are taken for the usual variations of room temperature which influence the sixth decimal place of the refractive index.

† Shown experimentally, p. 196 of footnote 1.

‡ The lower limit of the transformation region will be called T_a and the upper limit T_β.

that is dominated by two factors, (*a*) the distribution of the speed of transformation and (*b*) the temperature, T_a. At the upper limit of the transformation region, the glass reaches its equilibrium practically instantaneously. On the other hand, even if no attention is given to the structural equilibrium of glass, the speed of cooling is limited by the maximum gradient of temperature which the glass can stand without breaking. The speed of cooling will thus remain less than the speed of transformation down to a certain temperature, T_1; above T_1, the cooling will automatically keep the glass in a state of equilibrium.

To maintain the equilibrium below T_1 is a time-consuming process which should be dispensed with whenever possible. This can be done by taking advantage of the cause of this additional time required for annealing, namely, the decrease of the speed of transformation.

Because the speed of transformation near T_a is very low, a sample of glass, after it has reached equilibrium in the whole volume at a certain temperature $T_e > T_a$, can be cooled from there rapidly enough not to undergo any appreciable transformation during the cooling. The sample will thus be brought to a temperature, $T_f < T_e$, at which it is no longer in equilibrium, practically without affecting its homogeneity. At T_f, the speed of transformation is still lower than at T_e; thus, after the "freezing" process has ended, further cooling from T_f to room temperature can be at slower, more practicable rates.

It is to be emphasized that the cooling rate does not need to undergo any sudden change at T_f; the variation of temperature can be continuous from T_e to room temperature if the cooling rate at each temperature is rapid enough to avoid any further transformation of glass. This freezing of glass in a certain state of equilibrium, corresponding to T_e, represents a gain of time necessary to anneal the glass from T_e to the lower limit of the transformation region, T_a. This effect may be important because the time necessary to reach equilibrium increases exponentially as the temperature decreases.

The higher the temperature, T_e, the greater is the gain in time. Two conditions, however, limit the value of T_e as follows: (1) The transformation rate at T_e should be slow enough to permit freezing when a certain speed of cooling is imposed by the other conditions. (2) For a given glass, T_e will vary with the size of the sample because the inside of the piece of glass during a cooling period is hotter than the outside and the transformation rate inside is greater than that on the outside. To be able to freeze a sample of glass which is in a state of equilibrium without disturbing the existing homogeneity, it should be possible to neglect the transformation of the hottest part of the sample during rapid cooling.

Although, as stated previously, the rate of cooling does not need to undergo any sudden variation at any particular temperature, T_f, it is often convenient in practice to apply such a change. For example, instead of providing a special cooling rate, it may be easier to remove a sample from a furnace at temperature T_e and place it in a furnace at temperature T_f and then to cool with the furnace.

The choice of T_f depends on the cooling rate that is to be applied after the freezing process, $T_e \rightarrow T_f$, is completed. The transformation rate at T_f must be slow enough to give only a negligible change in the glass during cooling from T_f to the final temperature of use.

The fulfillment of these conditions gives a structurally homogeneous sample of glass that at room temperature is not entirely stabilized. Although exact figures on the speed of aging at room temperature are not available, this phenomenon is known to be very slow. Furthermore, if the glass is homogeneous, its variation with time will be the same throughout its mass. The deformation of the surface and spontaneous breakage will thus be averted.

Owing to the tremendous difference in the transformation rate over the transformation region, only part of this region is interesting from a practical viewpoint. The vicinity of the upper limit is unimportant because the speed of transformation is higher than that of cooling allowed by other considerations, such as the temperature gradient. In the vicinity of the lower limit of transformation region, the speed is so low that it permits the freezing process to take place.

The exact determination of the lower limit of the transformation region is unimportant when the freezing process is to be applied, but it is essential when the limit annealing is needed. In this case, the lower limit of the transformation region coincides with T_e and T_f of the freezing process. Once a glass is obtained in equilibrium at the lower limit of the transformation region, it may be cooled further at any desired speed if it can stand the rate without breaking because below the transformation region, structural equilibrium will be reached simultaneously with thermal equilibrium.

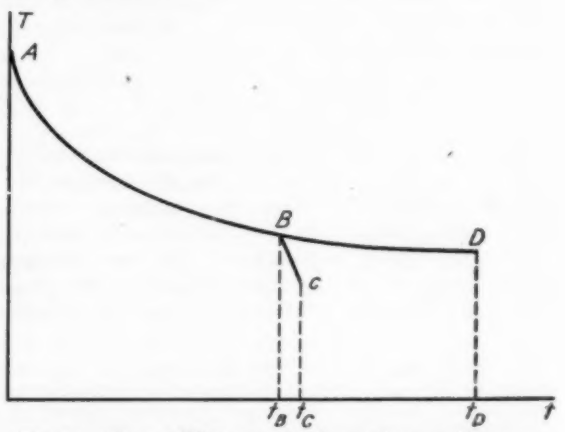

FIG. 1.—Curve *ABD*, general form of annealing curve based on transformation phenomena; *BC*, period of rapid cooling when freezing process is applied.

The freezing method can be represented by the annealing curve *ABC* in Fig. 1. Two parts of this curve may be distinguished; *AB* follows the transformation of the glass and *BC* is the proper freezing portion. At point *B*, the glass is in equilibrium corresponding to

the temperature T_B; at point C, the glass still remains in a state of equilibrium corresponding to T_B. The gain in time as compared to the limit annealing is $T_C - T_D$.

The foregoing discussion gives the answer to the problem formulated in section II, that is, it gives the method of annealing resulting in glass that is structurally homogeneous although not entirely stabilized, and it shows that a considerable gain of time can be realized with respect to the time of limit annealing. The importance of this gain in time depends on the particular problem involved, for example, the quality of the annealing and the size of the pieces to be annealed.

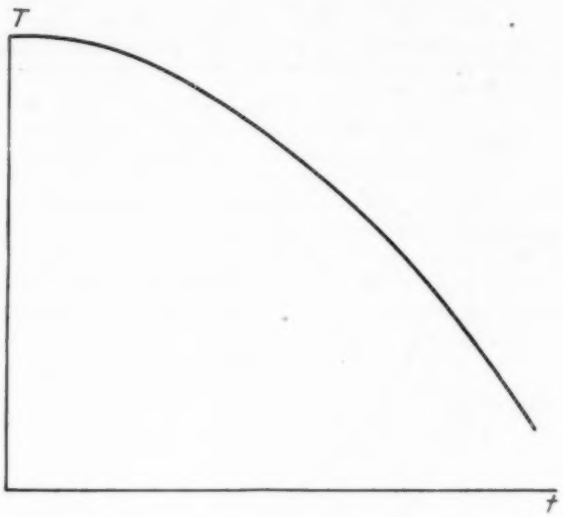

FIG. 2.—Usual form of annealing curve.

The proposed annealing schedule differs considerably from that most frequently applied in practice, which is represented by the curve in Fig. 2. Two objections that can be made to this form of the curve are as follows: (1) It does not take advantage of the fact that equilibrium is attained more quickly at higher temperatures, and (2) it leads more readily to a lack of structural homogeneity because the temperature gradient increases with the rate of cooling, and, therefore, for this curve it is steeper at the end of the annealing period than at the beginning.

The reverse is true for the curve of Fig. 1. Since the cooling rate diminishes as annealing progresses from A to B and D, the gradient steadily diminishes. The only required precaution is that equilibrium be reached in the entire volume of glass at the lowest temperature that determines the final equilibrium of the annealing. This temperature of final equilibrium corresponds on Fig. 1 to D for the limit annealing (and coincides with T_a) and to B when the freezing process is to be applied.

Another conclusion to be derived from this phenomenon is to be emphasized. If the time available for annealing a sample is shorter than that needed for a limit annealing, the best result will not be obtained by speeding up the cooling rate indiscriminately. The correct procedure is to follow the same schedule as for the limit annealing during the time available and then, if possible, to apply the freezing process. If the latter process cannot be used, the sample should be cooled with a maximum possible speed down to the temperature of use. This procedure will yield a more homogeneous glass than an all-over speeding up of the cooling rate.

The foregoing procedures, which indicate how to obtain the best use from the available annealing time, apply to all kinds of glass. Optical glasses require a structural homogeneity because its lack may introduce aberrations. For other glasses, a structural homogeneity is important because of the requirements of homogeneity of mechanical constants, such as specific volume and coefficient of expansion.

V. Numerical Values

The order of magnitude of different constants involved must be considered in order to obtain further practical conclusions from the described behavior of glass. The transformation region probably spreads over some 200°C. for different glasses. Few experimental data are available, and the upper limit is difficult to determine owing to the extremely high rate of transformation in this region. This high transformation rate, however, makes the upper part of the transformation region unimportant for practical purposes.

Table I gives the lower limit of the transformation region, T_a, for several glasses.

TABLE I

APPROXIMATE LOWER LIMIT (T_a) OF TRANSFORMATION REGION

Glass	T_a
DF	340°C.
LF	350
EDF	375
BSC	480
BCD	500

The part of the transformation region important for annealing is that part in which an appreciable time is needed to reach equilibrium. To give an order of magnitude, the highest practically important temperatures are those that require one or two hours to reach equilibrium. The extent of this annealing range varies from 50°C. for glasses which are easy to anneal to 75°C. for those more difficult to anneal; the latter value is rarely exceeded.

Experiments show that glasses with a longer annealing range are those for which the transformation rate (or parameter B) diminishes more rapidly with temperature in the lower part of the transformation region; a broader annealing range, therefore, does not necessarily mean a longer annealing time, but it does require greater care in the determination of the annealing schedules. A small error in temperature more seriously affects annealing of glasses that have wide annealing ranges.

When a sample of glass is taken at temperature T_1, near the upper limit of the transformation region, at

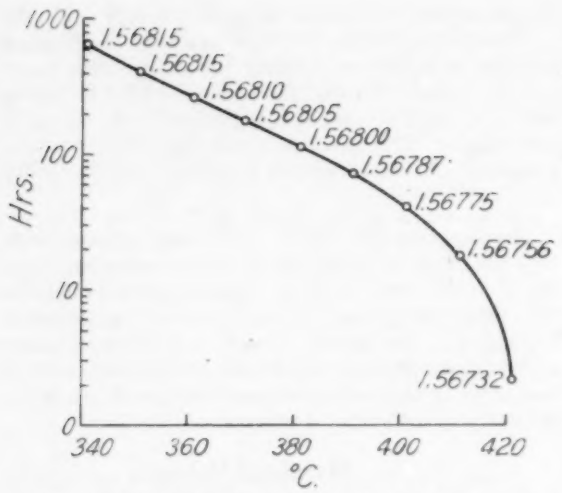

FIG. 3.—Curve showing time needed to reach an isothermal operation, as function of temperature at which this operation is performed.

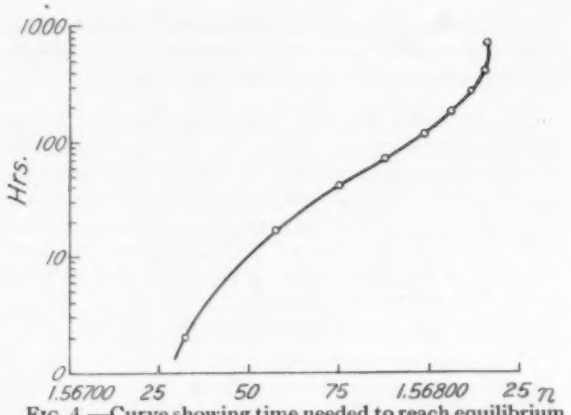

FIG. 4.—Curve showing time needed to reach equilibrium in an isothermal operation as function of refractive index of equilibrium.

which it is in equilibrium, and is cooled rapidly to another temperature T_2, the time needed to reach equilibrium at T_2 will be a few minutes when T_2 is about 100°C. above T_a, a few hours if T_2 is about 50°C. above T_a, and several hundred hours when T_2 is near T_a.

All values given in this section indicate only an order of magnitude; exact numerical values for one typical kind of glass will therefore be interesting. The values to be given correspond to a light flint glass used in optics. The physical constant that represents the state of glass is its refractive index (the most important constant for optical uses); all measurements of refractive index are made at room temperature (about 20°C.) to represent the behavior of the glass in the condition of use.* The glass is considered to have reached equilibrium if the variation of the refractive index is smaller than 2×10^{-5}. The selected flint glass has the following characteristic data:

$T_a = 351$°C.
$n_{max.}$ (corresponding to limit annealing) = 1.56815.
$n_{min.\ observed}$ (sample chilled from 450°C.) = 1.56545.
$\Delta n = n_{max.} - n_{min.} = 2.7 \times 10^{-3}$.

The most important data needed for the determination of an annealing schedule are the rates of transformation. Figures 3 and 4 give the times required for reaching equilibrium as obtained from the curves of isothermal transformation of the chosen flint glass.†

The curves of Figs. 3 and 4 correspond to a sample that was brought to equilibrium initially at T_1 = 450°C. Figure 3 shows the time required for the sample to reach equilibrium in an isothermal operation at T_2 (indicated by the abscissa of the curve). For each experimental value of T_2, the corresponding value of n_T is inscribed. The curve in Fig. 4 is obtained from Fig. 3 by plotting n_T as the abscissa instead of T_2. Figure 3 shows that the annealing range for this glass extends

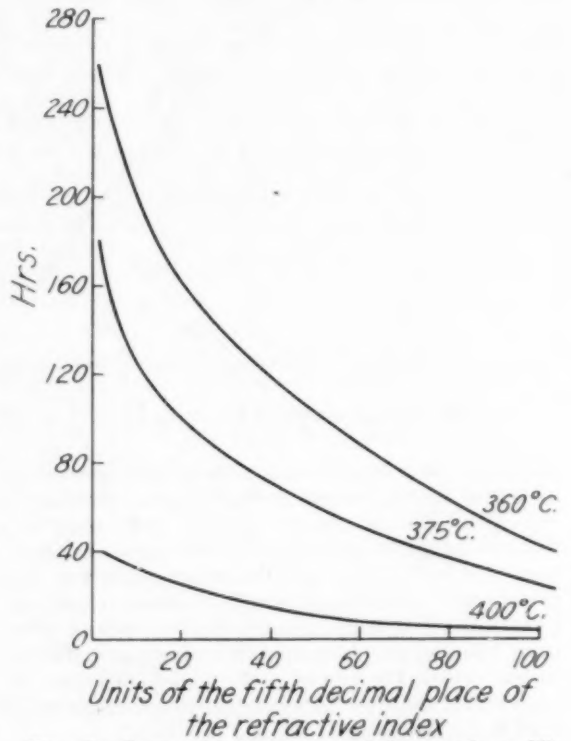

FIG. 5.—Curves showing time needed to reach equilibrium as a function of precision with which the index of equilibrium is to be reached (for three isothermal operations.)

from about 420° to 351°C., that is, to T_a. The rate of transformation continues to decrease steadily with the temperature below T_a. Figure 4, however, shows that the refractive index remains the same for temperatures below T_a.‡

If n_T is to be reached with a precision of less than 2×10^{-5} as required (Figs. 3 and 4), the required time is also

* See p. 191 of footnote 1 for method of quenched samples.

† See Part III and Fig. 6, pp. 192–93 of footnote 1.

‡ The results are obtained by the method of quenched samples, previously referred to, which eliminates the instantaneous component of the variation of the refractive index.

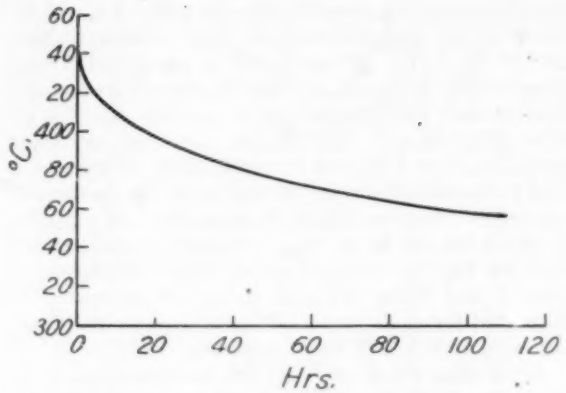

FIG. 6.—Annealing curve of the selected light flint glass.

less. Figure 5 shows the time needed to reach equilibrium at three different temperatures when the required precision decreases from 10^{-5} to 10^{-3}. The curves in Figs. 3, 4, and 5 also show that precise temperature control during the annealing process is of the utmost importance. If the actual temperature of the sample is higher than that read on the thermometer, the desired index, n_T, cannot be reached and too long a time will be allowed for reaching the actual refractive index. If the actual temperature is lower than the temperature read, the time required to reach n_T will be increased. Table II shows the amount of time lost, Δt, in an isothermal operation when the difference, ΔT, between the actual and the read temperatures is equal to $-3°$, $-5°$, and $-10°$C.

TABLE II

INCREASE OF ANNEALING TIME CAUSED BY ERROR IN TEMPERATURE

Temp. T (°C.)	Δt for ΔT (hr.)		
	-3°C.	-5°C.	-10°C.
420	4.5	6.5	11
400	9	16	30
380	20	35	70
360	40	80	150
350	50	100	280

VI. Details of Application of Freezing Method

It was pointed out that the freezing process can be applied to two types of problems. The first problem involves the attainment of the best possible annealing in a given length of time. This result is obtained by following the curve for limit annealing (given for the chosen glass on Fig. 6) during the entire available time and then applying the freezing process. Thus T_s,[§] at which the freezing process starts, is automatically determined by the available time. The rate of cooling during the freezing and (if a discontinuous rate of cooling is to be applied) the end temperature, T_f, remain to be determined.

§ As explained in section IV, the temperature T_s is to be maintained until the disappearance of any gradient of temperature in the volume of the sample. The last operation secures the homogeneity of the sample inasmuch as all points of the volume will reach equilibrium within the precision of 10^{-5} on the refractive index.

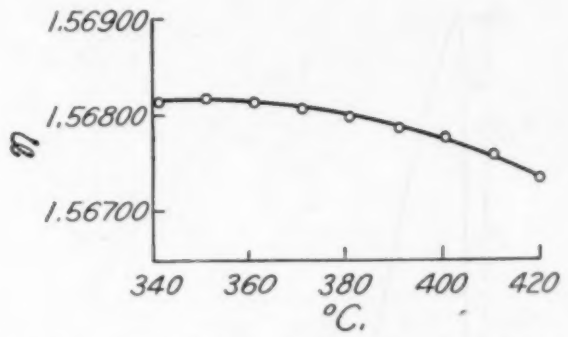

FIG. 7.—Curve showing refractive index of equilibrium of a light flint glass as a function of the temperature (obtained by method of quenched samples).

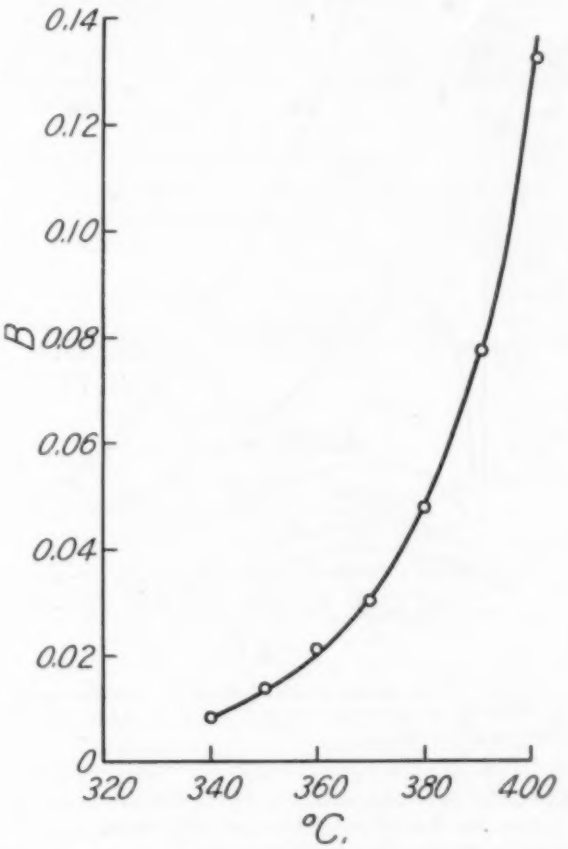

FIG. 8.—Curve showing B as a function of temperature for the light flint glass.

In the second problem, a desired degree of stabilization of glass (that is, the maximum difference, Δn, between the index to be obtained and the index of limit annealing) is to be obtained in the shortest possible time. This result is obtained by following the curve of limit annealing until T_s is reached, at which temperature the index of equilibrium is the desired index, and then by applying the freezing process. Thus T_s is automatically determined by the value of the refrac-

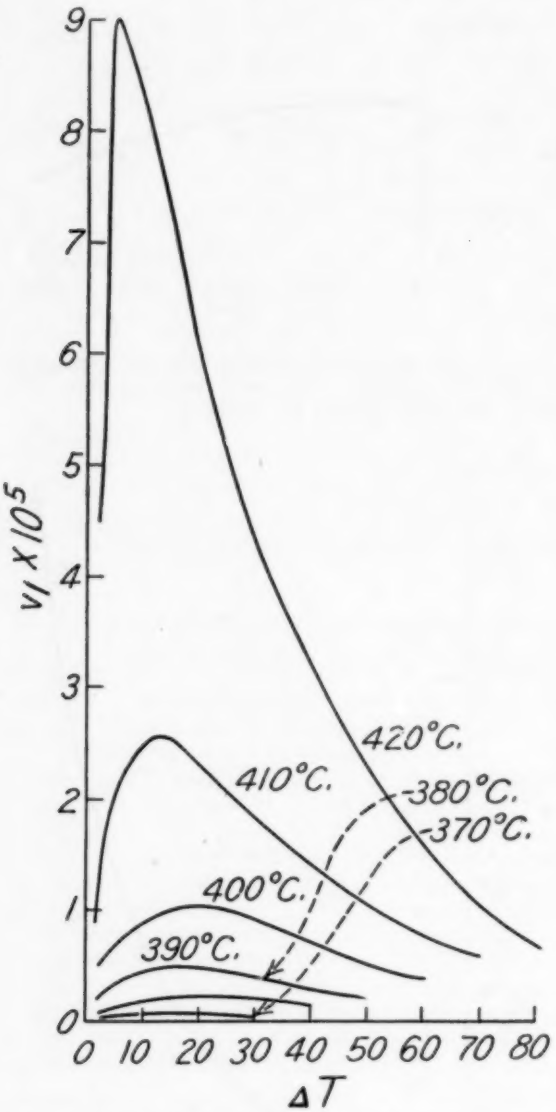

FIG. 9.—Curve showing initial speed of transformation for different temperatures as a function of magnitude of temperature drop.

tive index to be obtained. As in the first problem, the cooling rate during freezing as well as T_f must be determined if a discontinuous rate of cooling is to be applied.

The precise determination of each of these quantities requires a knowledge of the transformation rate during a cooling that is a nonisothermal operation. The writer has been unable to find any definite information on this "dynamic" rate of transformation; for this reason, the following approximation method will be used:

During an isothermal operation, the greatest speed of transformation is the initial rate, v_i, given by equation (3) (see p. 267). If a sample of glass, taken at T_0 at which it was in equilibrium (index $= n_0$), is brought instantaneously to T' (index of equilibrium $= n_T$) and is maintained at this temperature, the value of v_i will depend on the magnitude of the drop in temperature, $\Delta T = T_0 - T'$. If the variation of n_T and B with temperature is known, v_i may be plotted as a function of ΔT for different values of T_0; $n_T = f(T)$, $B = g(T)$, and $v_i = h(\Delta T)T_0$ are given for the chosen glasses in Figs. 7, 8, and 9, respectively. The curve of Fig. 7 was obtained from the curves of the isothermal operation*; that for Fig. 8 was calculated by equation (1) from the curves of the isothermal operation; and that for Fig. 9, by equation (3) from data shown in Figs. 7 and 8 for different initial temperatures, T_0, indicated for each curve. Figure 9 shows that each curve, $v_i = h(\Delta T)T_0$, has a maximum ($v_{i\,max}$).

If the glass transforms with this maximum speed, the maximum time, t_m, during which a sample can be maintained at a given temperature before the variation of the refractive index attains a given value, δn, can be deduced from Fig. 9. In Fig. 10, t_m is given as a function of temperature for $\delta n = 1 \times 10^{-4}$, $\delta n = 1 \times 10^{-5}$, and $\delta n = 1 \times 10^{-6}$. It seems safe to assume that the speed of transformation during the nonisothermal operation will not exceed the value, $v_{i\,max}$, given in Fig. 9. The degree of transformation in the hottest part of the glass, therefore, will not exceed δn if each temperature during the cooling period is reached in a time no longer than that given by the curve of Fig. 10 for this temperature and for this δn.

The variation of temperature inside a sample of glass, when the outer surface is cooled at a given rate, has been theoretically investigated by Williamson and Adams.[4] In practice, rough experimental determination is sufficient because the cooling rate of the outer surface in most cases can be chosen so as to provide a wide margin of safety.

The cooling rate of the hottest part of a sample of a given size obviously increases with the cooling rate of the outer surface (or with the difference, $T_e - T_f$). The only limit to the cooling rate of the outer surface (or to the magnitude of $T_e - T_f$) is the maximum speed of cooling that the sample can stand without breaking. This maximum speed has been determined by Adams and Williamson[5] who state, "in order to allow a fair factor of safety, optical glass should never be cooled at a rate greater than $10/a^2$°C. per minute, a being the semithickness of the slab."

It will be found in practice that for samples of the usual size and with T_e not too high, the limit of speed imposed by the Adams and Williamson formula is much larger than the cooling rate of the outer surface necessary to satisfy, in the hottest part of the glass, the condition imposed by Fig. 10. As the cooling progresses, the speed of transformation diminishes and the cooling rate can be still lower. In other words, in the usual condition of practice, the formula of Adams and Williamson[5] does not constitute any obstacle for the application of the freezing process.

* See Part III and Fig. 6, pp. 192–92 of footnote 1.

[4] E. D. Williamson and L. H. Adams, "Temperature Distribution in Solids During Heating or Cooling," *Phys. Rev.*, Series II, **16**, 99–114 (1919).

[5] L. H. Adams and E. D. Williamson, "Annealing of Glass," *Jour. Franklin Inst.*, **190** [6] 869 (1920).

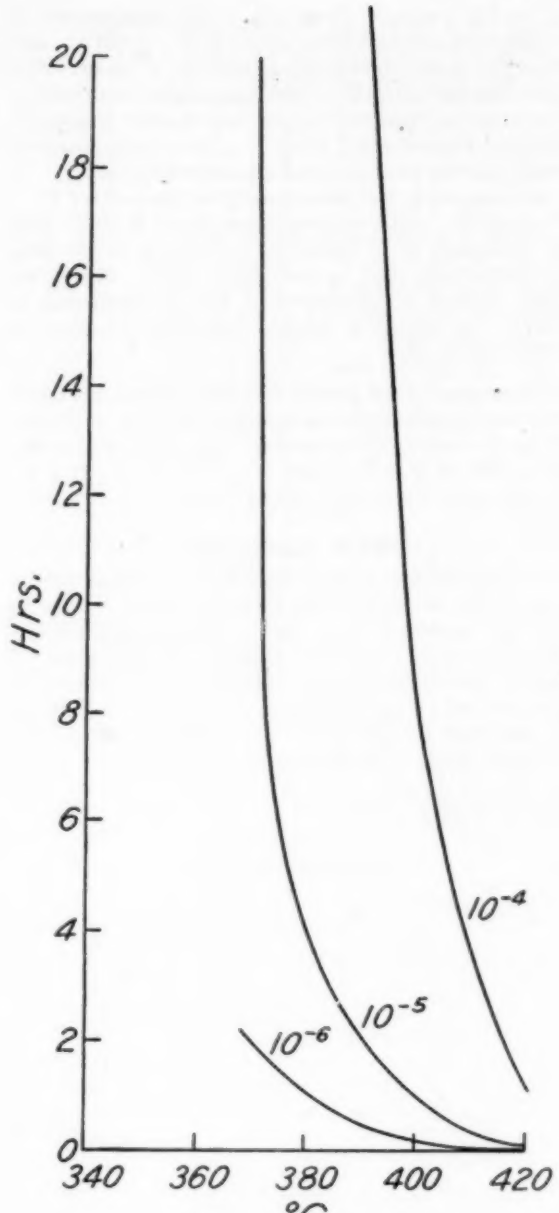

FIG. 10.—Curves showing maximum time during which the glass will keep a given degree of homogeneity as function of temperature at which glass is maintained.

If the discontinuous freezing process is to be applied, T_f, will be determined simply by the condition that the transformation speed at T_f be low enough to give a margin of safety during subsequent cooling from T_f to room temperature. The corresponding $T_e - T_f$, in practice, will then automatically give a sufficient rate of cooling during the freezing process.

VII. Examples of Discontinuous Freezing Method

Two examples will be given for the previously chosen light flint glass to show how the data necessary for the application of the freezing process can be determined, even for rather stringent requirements of stability and homogeneity.

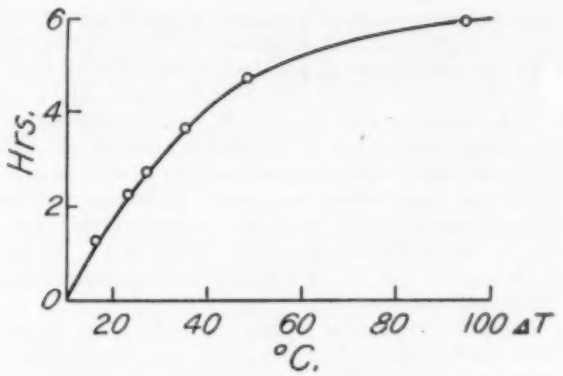

FIG. 11.—Curve showing time needed for sample A to reach thermal equilibrium when submitted to rapid variations of temperature (see example (*A*)).

(1) Time Allowed for Annealing

The temperature of equilibrium reached after 20 hours of annealing is $T_e = 400°C.$ (taken from Fig. 6). The corresponding refractive index of equilibrium (from Fig. 7) is $n_T = n_{400°C.} = 1.56778$ and $n_{max.} = 1.56815$; therefore, $\Delta n = n_{max.} - n_T = 3.7 \times 10^{-4}$. From Fig. 10, the minimum speeds of cooling for the hottest part of the sample at the beginning of the freezing period* would be as follows:

14°C./hr. to guarantee homogeneity $\delta n = 1 \times 10^{-5}$.

1.5°C./hr. to guarantee homogeneity $\delta n = 1 \times 10^{-4}$.

Two samples, A and B, were investigated and are described in examples (*A*) and (*B*).

Example (*A*): Cylindrical plate, 12 cm. in diameter, 3 cm. thick; maximum cooling rate by the Adams and Williamson formula,[5] 4°C. per minute; for reasons of practical convenience, this rapid cooling rate could not be maintained longer than 10 minutes so that $T_e - T_f \gtrsim 40°C.$ The cooling rate for the hottest part of the sample, corresponding to a given T_f, was approximately determined by the following method: The plate was submitted to sudden variations of temperature ΔT and the time, τ, necessary to reach thermal equilibrium was determined by the form of the surface.

The results (Fig. 11) show that when $\Delta T = T_e - T_f = 40°C.$, $\tau = 4$ hours, that is, the average cooling speed of the hottest part of the sample is equal to 10°C. per hour.† Although the initial cooling rate is much faster than the average, it is difficult, if not im-

* The speed of cooling is given by the slope of the tangent of the chosen curve of Fig. 10 for the given temperature T_e.

† It was found necessary to have a large coefficient of security for the rate of cooling obtained by this rough experiment; the cooling was performed in air, and it was observed that quite an appreciable amount of time passes before the surface of the glass takes the actual temperature and the maximum gradient of temperature appears in the glass sample.

possible, in this case to guarantee the homogeneity of $\delta n = 1 \times 10^{-5}$. The homogeneity of 1×10^{-4} on the refractive index can be obtained easily even if $T_e - T_f < 40$°C.

If, for example, $T_e - T_f = 10$°C., Fig. 11 shows that the sample will reach its thermal equilibrium in less than one hour; this gives an average cooling rate of 10°C. per hour, which is greatly in excess of that needed, that is, 1.5°C. per hour. At temperature T_f = 390°C., the transformation rate (given in Fig. 10 for $\delta n = 1 \times 10^{-4}$) is 1°C. per hour, which determines the subsequent cooling rate.

Example (B): Size of sample, 2 by 1 by 1 cm.; maximum permissible cooling rate, 40°C. per minute (from Adams and Williamson). Because this sample is much smaller than sample A, the hottest part will follow the temperature much more rapidly than in the previous case. Since Fig. 11 indicates, for a large sample, an average cooling rate of 10°C. per hour for $\Delta T = T_e - T_f = 20$°C., it is safe to assume for a small sample that the same value of $T_e - T_f$ will give for the hottest part a cooling rate that is larger or equal to 14°C. per hour. The homogeneity will thus be $\delta n = 1 \times 10^{-5}$.

For $T_f = 380$°C., the transformation speed, as given in Fig. 10, for $\delta n = 1 \times 10^{-5}$, is equal to 3.5°C. per hour, this determines the initial cooling rate from T_f to room temperature.

(2) Required Refractive Index

The difference between the required refractive index of n_T 1.56800 and this limit of annealing is $\Delta n = n_{max.} - n_T = 1.5 \times 10^{-5}$. From Fig. 7, the temperature of equilibrium corresponding to n_T is $T_e = 380$°C., and from Fig. 6, the corresponding time is $t = 50$ hr. Figure 10 shows that at $T_e = 380$°C., the minimum cooling rate must be equal to 3°C. per hour in order to guarantee a homogeneity of 1×10^{-5}. This cooling rate is so small that the freezing process is extremely easy.

For sample A, this homogeneity is obtained for $T_e - T_f = 10$°C., and the temperature drop of 10°C. may be performed in 2.5 minutes. For sample B, the drop in temperature may be even more rapid. The subsequent cooling is determined by the condition that at 370°C. the minimum cooling rate must be equal to 0.3°C. per hour.

Examples (1) and (2) illustrate the method described, but they do not represent the best conditions of its use. In many cases, such as example (1), the method may be improved if the cooling is started at T_e at a required speed and is then slowed down.

VIII. Conclusions

A considerable gain in annealing time can be obtained, not by seeking the highest refractive index or the best stabilized glass but by emphasizing the importance of structural homogeneity for the glass. A specific method of cooling permits freezing into a homogeneous state a piece of glass that is not in equilibrium at the final temperature. Nevertheless, the glass is suitable even for precision uses.

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SUBSTITUTION OF TOPAZ, DOMESTIC KYANITE, AND SYNTHETIC MULLITE-CORUNDUM FOR INDIA KYANITE: IV, RAW TOPAZ AS HIGH-TEMPERATURE BOND FOR DOMESTIC KYANITE*

By T. N. McVay, W. W. Galbreath, Jr., and Dan Allen†

Abstract

Raw topaz has been found to act as a high-temperature bond for both raw and calcined kyanite. It is thought that this bonding action is due in part to volatiles which emerge from the raw topaz between 1000° and 1200°C. Some of the topaz decomposition products are absorbed and retained by the calcined kyanite. Within the limits of this investigation, all refractories which contained either calcined or raw kyanite, or mixtures of the two, with a minimum of 10% raw topaz had a good structure and were well bonded. The results of the load tests indicated that increased firing temperatures in the preheat improved the load resistance, but excellent high-temperature resistance was obtained by preheating as low as 1300°C. in laboratory kilns.

I. Introduction

In the course of a previous investigation[1] to find a domestic substitute for India kyanite, it was found that raw South Carolina topaz furnished an excellent bond for calcined domestic kyanite. Refractories made from these materials had a high pyrometric cone equivalent (P.C.E.) value, high mechanical strength after firing, excellent load resistance at elevated temperatures, and were comparatively volume constant on repeated firings. The present research was inaugurated to continue the exploration of the use of raw topaz with calcined and raw domestic kyanite as refractory materials.

II. Raw Materials

Two commercially prepared kyanite concentrates were used. Both raw and calcined kyanite A were furnished by the producer. Kyanite B received a special beneficiation for extra purity, and when a calcined B product was needed it was heated to 1500°C. in the Norris kilns. The analyses are given in Table I.

The microscopic examinations showed that the principal impurity in kyanite A was quartz with some rutile. Kyanite B contained a very small amount of free quartz.

The topaz was received raw from the Jefferson, South Carolina, deposit.

(1) Preparation of Specimens for Preliminary Tests

Small test pieces, 1 by 2 by 0.75 in. in size, were used in all preliminary work. The batches were accurately weighed, 2% powdered gum arabic was added as a binder, and, after mixing with the proper amount of water, the specimens were pressed at 7500 lb. per sq. in. Unless otherwise indicated, all specimens were heated for 4 hours at 1500°C.

Table I

Analyses of Kyanites*

	A (%)	B (%)
Al_2O_3	58.42	61.16
SiO_2	38.12	37.98
Fe_2O_3	0.78	0.64
TiO_2	1.30	0.0
CaO + MgO	0.25	No data
Ignition loss	0.12	No data†
	98.99	99.78
Theoretical kyanite	92.6	97.2

* Analyses by H. R. Shell and L. R. Mason, assistant chemists, U. S. Bureau of Mines.
† Ignited sample.

Table II

Composition of Bodies

No.	Composition	Parts
1	Raw kyanite	100
2	Raw kyanite	50
	Topaz calcined above 1400°C., −100-mesh	40
3	Raw kyanite	50
	Raw topaz, −100-mesh	50
4	Calcined kyanite	100
5	Calcined kyanite	50
	Raw topaz, −100-mesh	50

III. Volume Expansion and Porosity of Kyanite and Topaz-Kyanite Bodies

The kyanites were carefully screened into six fractions as shown in Figs. 1, 2, 3, and 4 with practically no fines present in a given fraction. Compositions of the bodies are shown in Table II.

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* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, April 5, 1944 (Refractories Division). Received March 13, 1944.

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[1] T. N. McVay and Hewitt Wilson, "Substitution of Topaz, Domestic Kyanite, and Synthetic Mullite-Corundum for India Kyanite, I–III," *Jour. Amer. Ceram. Soc.*, **26** [8] 252–66 (1943).

Some of the preliminary experiments on the use of topaz as a binder for both raw and calcined kyanite were made early in 1942 at the Eastern Experiment Station, Bureau of Mines, College Park, Md., by Alton Gabriel and Howard F. Carl.

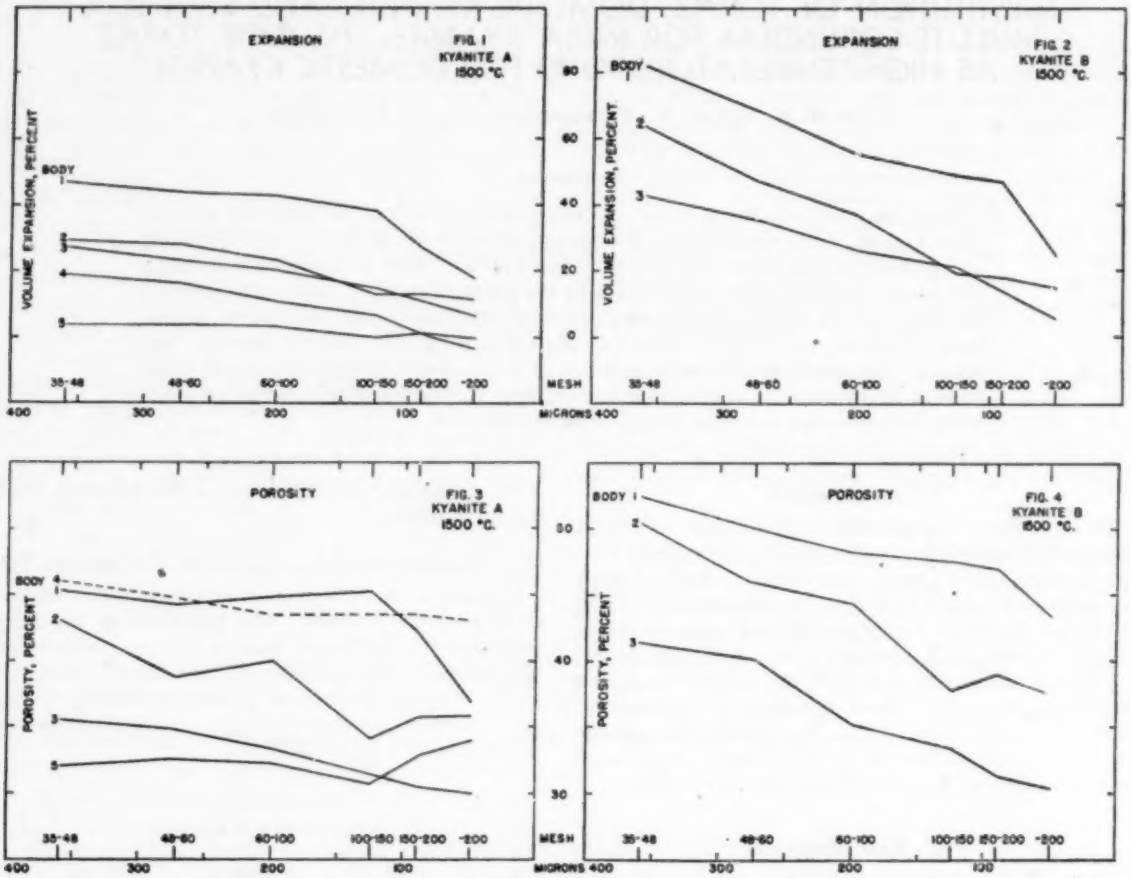


FIG. 1.—Volume expansion of bodies containing kyanite A at 1500°C. FIG. 2.—Porosity of bodies containing kyanite A at 1500°C. FIG. 3.—Volume expansion of bodies containing kyanite B at 1500°C. FIG. 4.—Porosity of bodies containing kyanite B at 1500°C.

Inasmuch as topaz loses about 20% in weight during firing, 40 parts of calcined topaz were used in composition No. 2 (Table II), this being equivalent to the weight produced by 50 parts of raw topaz after firing. Kyanite A was used in all five mixtures and kyanite B in the first three compositions of the series shown in Table II. The volume changes in firing are given in Figs. 1 and 2 and the porosities in Figs. 3 and 4. These are the average results of measurements on three test specimens of each composition.

(1) Results

Raw kyanite B had a greater volume expansion than raw kyanite A, especially with the coarser fractions. Microscopic examination of the raw kyanites gave no evidence that could account for this difference because each grain, irrespective of its size, consisted of a single crystal fragment. The smaller particle sizes of both kyanites showed less expansion. This was probably due to less exfoliation of the smaller crystals during inversion. Raw topaz, when mixed with the coarser kyanite fractions, caused a greater decrease in volume expansion than calcined topaz. This decrease was more marked in kyanite B.

What is more important, all specimens containing raw topaz were well bonded, whereas those containing the calcined topaz were weak and friable. Other test specimens, not included in Figs. 1 and 2, containing 100% of −100-mesh calcined topaz, had a volume shrinkage of about 3%, whereas raw topaz specimens of the same fineness showed a volume expansion of about 2%. The low expansion of pressed topaz fines is of particular interest because the previous study[1] has shown that raw lump topaz had about 13% volume expansion when fired to 1500°C.

The volume expansion of the −35- +48-mesh fraction of commercially calcined kyanite A was 18%, probably due to incomplete inversion of the raw kyanite. The addition of raw topaz to the same fraction of calcined kyanite A lowered the volume expansion of the mixture to 4% or less.

As would be expected from the volume-expansion characteristics, kyanite B had a greater porosity than kyanite A. Body No. 3, which contained raw topaz, had much lower porosity than No. 2, which contained calcined topaz. The porosity curves of the raw kyanite-calcined topaz series are irregular, owing to cracks in the fired test pieces; the porosity curves, however,

TABLE III

COMPOSITIONS

No.	Raw topaz(%) −100-mesh	Calcined kyanite A (%) −35-mesh	Calcined kyanite A (%) −200-mesh
6	100		
7	10	90	
8	30	70	
9	50	50	
10	50		50

TABLE IV

IGNITION LOSS (%) OF TOPAZ AND TOPAZ-KYANITE BODIES

Body No.	A	B	C	D	E	F
6	2.30	2.02	21.50	19.50	19.50	0.0
7	1.83	1.80	3.32	1.52	15.20	22.1
8	1.95	1.85	7.13	5.28	17.60	9.7
9	2.02	1.88	11.30	9.42	18.84	3.4
10	2.06	1.92	11.20	9.28	18.56	4.8

Ignition loss of topaz at 700°C., 0.28.
Ignition loss of calcined kyanite at 700°C., 0.0.

A, test bars at 700°C.
B, organic bond at 700°C., corrected for ignition loss of topaz.
C, test bars at 1500°C.
D, test bars at 1500°C., corrected for bond (C–B).
E, calculated ignition loss of the topaz at 1500°C. based on topaz content of the bodies.
F, topaz vapors retained, % topaz ignition loss.

lie above those for the raw kyanite-raw topaz series.

(2) Porosity, Volume Change, and Specific Gravity of Calcined Kyanite-Raw Topaz

Commercially calcined kyanite A was carefully screened into the following fractions: −35- + 48-, −60- + 100-, −100- + 150-, −150- + 200-, and −200-mesh. These fractions were combined with −100-mesh raw topaz, and the specimens were prepared as previously described. The proportions of calcined kyanite and raw topaz are shown in Figs. 5, 6, and 7. The curves for all sizes of kyanite are similar, and some have been omitted in order to gain clearness.

With two exceptions, an increase in raw topaz was accompanied by a decrease in porosity and volume expansion for all of the kyanite fractions. The raw topaz had little effect on the −150- + 200-mesh kyanite fraction, whereas the addition of raw topaz to the −200-mesh kyanite caused a slight shrinkage.

In general, the bulk specific gravity increased with increasing raw topaz content up to 40%.

IV. Retention of Decomposition Products of Topaz by Calcined Kyanite

Because raw topaz acts as a high-temperature bond for both raw and calcined kyanite, it was thought desirable to determine whether kyanite-topaz compositions retained some of the volatile topaz decomposition products.

The compositions used are shown in Table III. Two per cent gum arabic was added to each batch and five small bars, about 1 by 2 by 0.7 in. in size, of each composition were pressed at 7500 lb. per sq. in. These were dried at 110°C., allowed to come to equilibrium with the moisture in the air at room temperature, and then weighed to the precision of 1 mgm. Two of the bars of each composition were fired at 700°C. in order to determine the ignition loss caused by the presence of the bond. Ignition losses of the topaz and calcined kyanite

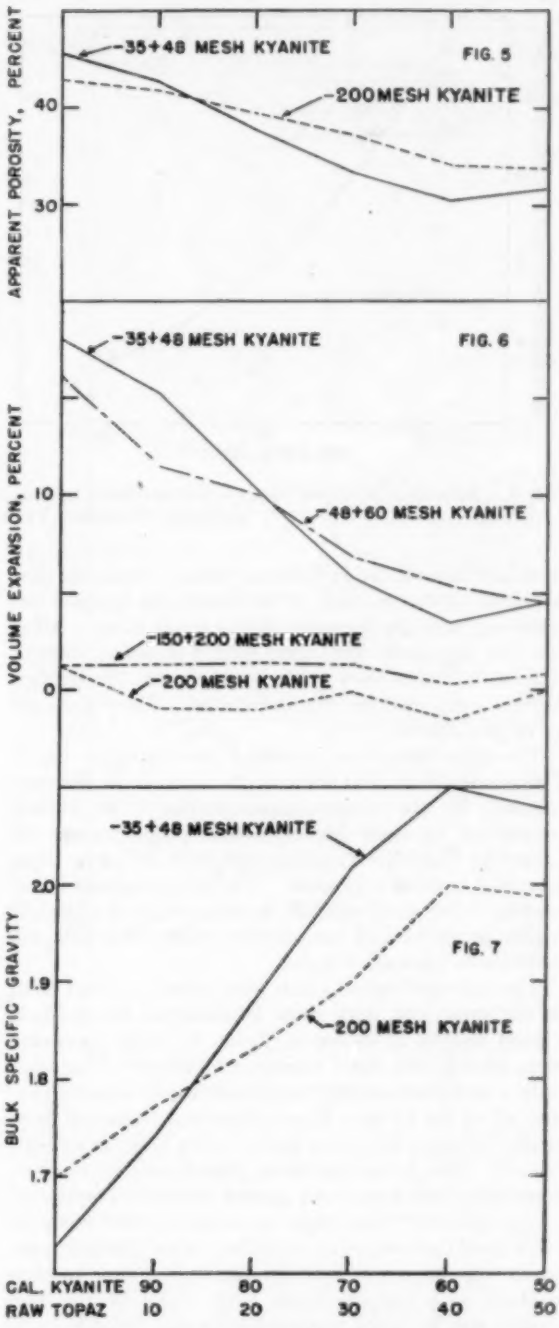
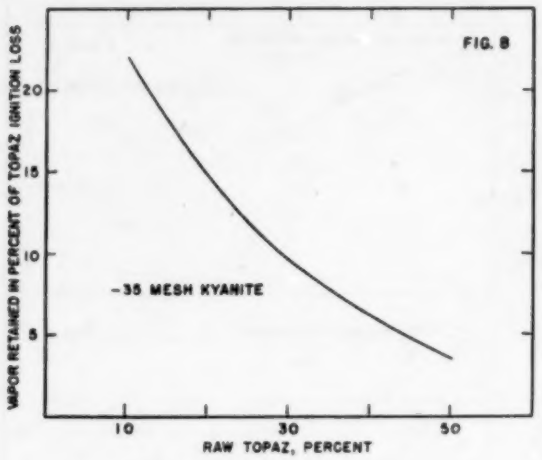


FIG. 5.—Porosity of calcined kyanite-raw topaz compositions. FIG. 6.—Volume expansion of calcined kyanite-raw topaz compositions. FIG. 7.—Specific gravity of calcined kyanite-raw topaz compositions.



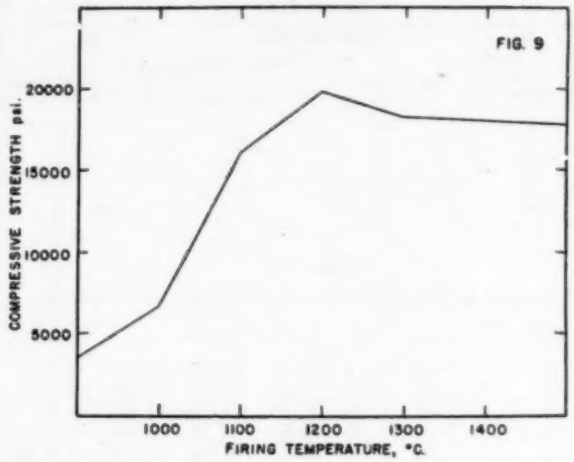


FIG. 8.—Retention of topaz composition products by calcined kyanite. FIG. 9.—Effect of temperature on compressive strength of calcined kyanite-raw topaz compositions.

were also determined in the same firing. From the data obtained, it was possible to determine the ignition loss resulting from the presence of the topaz alone. All of the test specimens were then fired 4 hours at 1500°C. After corrections were made for the gum, the ignition loss for each mixture was calculated. These data are given in Table IV.

The data taken from column F are plotted in Fig. 8. The results show that some of the topaz volatiles were retained by the kyanite-topaz bodies. The highest proportion of such decomposition products was retained by body No. 7, which contained 10% raw topaz and 90% calcined kyanite. The test specimens containing −200-mesh calcined kyanite retained a slightly higher proportion of the volatiles than those with the −35-mesh calcined kyanite.

The test specimens, which were given a second firing in the same kiln with some kyanite-raw topaz brick, gained weight as shown in Table V. The specimens were fired for the third time in a kiln, which contained only a few bars made from a raw topaz composition, and all of the kyanite-topaz specimens remained practically constant in weight except those made from body No. 10. The latter had been placed next to the bars containing raw topaz and gained weight. The experiments indicated that topaz or topaz-kyanite compositions would absorb topaz volatiles; all of the test specimens were therefore fired for the fourth time in close contact with kyanite-topaz brick. All of the bars gained weight, thus proving that topaz volatiles were absorbed. The writers have noted that test pieces containing 100% calcined kyanite gained in strength when they were fired in a kiln which contained raw topaz. Chemical and spectrographic analyses were made of the fired test pieces which contained topaz, and only a trace of fluorine could be detected.

It was thought that some of the bonding action of topaz might be due to hydrogen fluoride attacking the kyanite and forming aluminum fluoride, which might act as a flux. This theory, however, was disproved by adding from 2 to 10% of aluminum fluoride to calcined kyanite and firing bars made from these mixtures. None of these compositions was well bonded.

TABLE V

RETENTION OF TOPAZ VOLATILES (%) BASED ON SPECIMEN WEIGHT AFTER FIRST FIRING*

Body No.	Firing No. 2	3	4
6	0.087	0.089	0.496
7	.087	.088	.502
8	.060	.058	.388
9	.125	.123	.455
10	.082	.210	.610

* Firing temp., 1500°C.; results based on five test specimens of each composition.

When raw lump topaz is fired, silica glass is formed on the outside surfaces of the pieces. It is also known that calcination of topaz reduces the silica content of the raw mineral.[2] With bars made from topaz and combinations of raw and calcined kyanite fines, little glass formed on the exterior surfaces, especially when the raw kyanite content was low. At least part of the bonding action of topaz, therefore, is believed to be due to the deposition of silica glass in the pores of the refractory.

V. Temperature of Bonding Action

Experiments with both standard and small-sized brick showed that raw topaz has the property of bonding calcined and raw kyanite with or without clay additions. In order to determine the temperature at which this bonding occurred, small 1- by 2- by 0.6-in. test pieces were pressed on the flat at 7500 lb. per sq. in. These had a composition of 50% each of −48-mesh calcined kyanite A and −100-mesh raw topaz with 2% gum arabic added as a binder. Fifty test pieces were fired in sets of ten to 900°, 1000°, 1100°, 1200°, and 1300°C., respectively, and the temperature held 2

[2] R. S. Bradley, F. W. Schroeder, and W. D. Keller, "Study of Refractory Properties of Topaz," *Jour. Amer. Ceram. Soc.*, **23** [9] 265–70 (1940).

hours; a sixth set was fired at 1500°C. for 4 hours. The compressive strengths were determined and the results plotted in Fig. 9.

The greatest increase in strength occurred between 1000° and 1100°C., and within this temperature range, a marked dissociation of the topaz occurred with the evolution of volatiles. The cold compressive strength reached a maximum of nearly 20,000 lb. per sq. in. with those specimens fired at 1200°C. The reasons for the decrease of compressive strength with pieces fired above this temperature are not known. As bonding takes place at a comparatively low temperature, it may not be necessary to fire refractories made from well-calcined kyanite and raw topaz at extremely high temperatures inasmuch as excellent bonding was obtained by firing at 1200°C. Little volume change from the dry-pressed condition was found by firing at 1200°, 1300°, 1400°, and 1500°C.

VI. Load Tests of Standard-Sized Kyanite-Topaz Brick

Previous attempts at Norris to use raw kyanite in clay-bonded refractories have produced a "punky" structure owing to the inversion of the kyanite in firing with the resultant increase in volume. Excellent structures, however, were produced from calcined kyanite and raw topaz or with combinations of calcined and raw kyanite with raw topaz. Because calcined kyanite is more expensive than raw kyanite, the use of the raw mineral has some economic importance.

The preliminary tests on the bonding of raw and calcined kyanite by raw topaz (Figs. 1 to 4) suggested that mixtures of raw topaz with either calcined or raw kyanite might have lower porosities and volume expansions than calcined or raw kyanite alone. To verify these results, standard-sized brick having the compositions shown in Table VI were mixed with water containing 1% of organic binder (based on batch weight), pressed at 7400 lb. per sq. in. dried, and fired 4 hours at 1500°C. The brick were then subjected to the variable (V) temperature load test,[1] and the pertinent data are given in Tables VII and VIII.

(1) Variable-Temperature Load Test

This method has been previously described,[1] but several modifications have been made in the presentation of data. The temperature was gradually increased in the load-test furnace at a regular rate while the brick were subjected to a load of 25 lb. per sq. in. The furnace was calibrated with a recrystallized silicon carbide brick, and the expansion with increase of temperature was measured. As shown in Fig. 13, the linear change was plotted as the ordinate (1 linear unit equals 0.5%), and the temperature as the abscissa (1 linear unit equals 100°C.). In the evaluation of the results, the temperature at which maximum expansion occurred just before shrinkage started was considered important. The selection of this temperature was difficult because the expansion curve over a considerable temperature range frequently approached a straight horizontal line. Such a horizontal line was drawn, showing an expansion of 0.1% below the maximum value. The

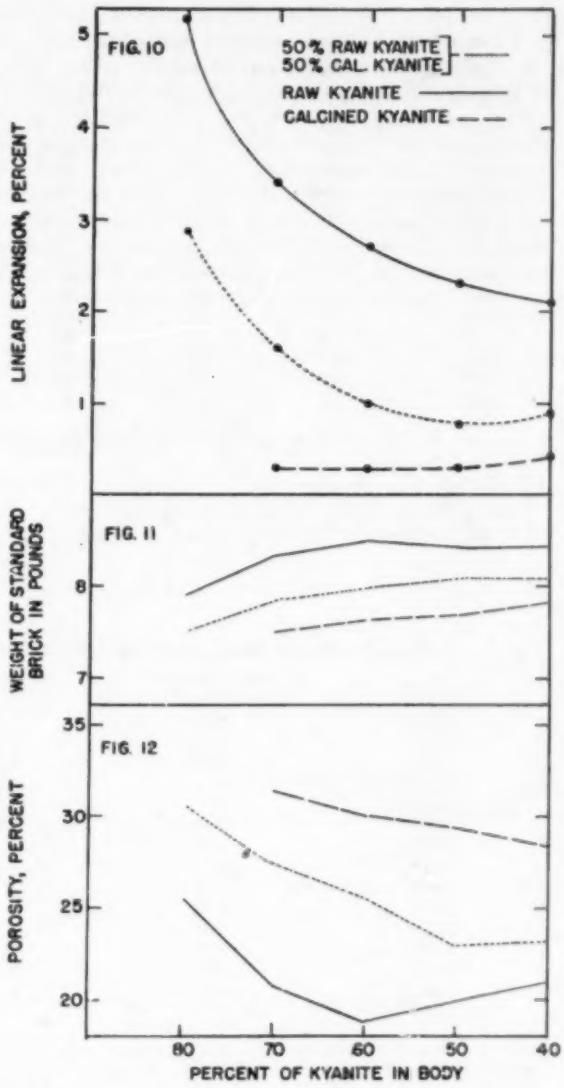


FIG. 10.—Linear expansion of kyanite-topaz brick after preliminary firing. FIG. 11.—Increase of weight of standard-sized brick with increase in kyanite content. FIG. 12.—Decrease in porosity with raw kyanite as compared with calcined kyanite.

two intersections of this line with the expansion curve gave what was designated as the temperature range of constant maximum expansion or that temperature interval in which not over 0.1% of linear change was found in the length of the test brick. With increased furnace temperatures as the brick approached failure, the expansion curve dropped rapidly. As a measure of this contraction, the temperature at which the slope of the expansion curve became 45 degrees was considered critical. At temperatures above the 45-degree tangent, the expansion was exceptionally rapid.

The maximum furnace temperature is the recorded temperature at the end of the test when the hot linear shrinkage had increased to about 1%; cold linear

TABLE VI

COMPOSITION OF TOPAZ-KYANITE BRICK (parts)*

Brick No.	Kyanite A (−35-mesh) Raw	Kyanite A (−35-mesh) Calcined	Raw topaz (−8-mesh)
200V	80		10
201V	70		20
202V	60		30
203V	50		40
204V	40		50
206V		70	20
207V		60	30
208V		50	40
209V		40	50
210V	40	40	10
211V	35	35	20
212V	30	30	30
213V	25	25	40
214V	20	20	50
			Calcined topaz −35-mesh
215V	70		16†

* Edgar plastic kaolin, 10 parts throughout.
† 16 parts calcined topaz = 20 parts raw topaz.

shrinkage figures are included as indications only because they have no comparative value unless all load tests are run to the same maximum temperature.

(2) Results

Figure 10 gives the linear expansions after the preliminary firing. Those brick that contained no calcined kyanite had the greatest linear expansion; calcined kyanite reduced the linear expansion as would be expected. Brick Nos. 201V and 215V contained 70% raw kyanite, the linear expansion of brick No. 215V, however, which contained calcined topaz, was much greater. This confirmed the results of the preliminary experiments that raw topaz reduces the expansion of raw kyanite. Brick No. 201V, which contained raw topaz, was superior in all respects to No. 215V, which contained calcined topaz.

All brick of this series that contained raw kyanite and raw topaz had good structures and were well bonded. Blisters were present on the outer surfaces of brick containing from 40 to 50% raw topaz when all

TABLE VII

KYANITE-TOPAZ REFRACTORIES AFTER PREHEAT TO 1500°C. (Properties Prior to Load Test)

Brick No.	Linear expansion in preheat (%)	Wt. standard brick (lb.)	Porosity (% of vol.)	Remarks
200V	5.2	7.9	25.5	Good
201V	3.4	8.35	20.9	"
202V	2.7	8.5	18.9	"
203V	2.3	8.45	20.0	Blistered
204V	2.1	3.45	21.0	"
206V	0.3	7.5	31.5	Good
207V	0.3	7.65	30.2	"
208V	0.3	7.7	29.6	"
209V	0.4	7.85	28.6	"
210V	3.0	7.50	30.8	"
211V	1.6	7.85	27.6	"
212V	1.0	8.00	25.7	"
213V	0.8	8.2	23.0	"
214V	0.9	8.2	23.3	Blistered
215V	8.5	7.0	36.1	Good

TABLE VIII

VARIABLE TEMPERATURE LOAD-TEST RESULTS

Brick No.	Temp. range of constant max. expansion (°C.)	Temp. 45° tangent (°C.)	Max. expansion hot (%)	Max. furnace temp. (°C.)	Linear shrinkage (%)	Wt. standard brick (lb.)	Porosity (% of vol.)
200V	920–1420	1510	0.60	1630	2.0	8.1	23.8
201V	940–1400	1560	.60	1635	1.9	8.5	19.2
202V	1100–1490	1590	.50	1635	1.7	8.7	17.6
203V	1160–1530	1570	.60	1670	1.9	8.7	17.6
204V	1130–1555	1570	.60	1675	1.3	8.6	19.1
206V	1020–1440	1515	.60	1625	2.5	7.7	30.3
207V	1100–1490	1520	.65	1615	1.7	7.7	29.8
208V	980–1490	1530	.60	1640	1.6	7.75	28.5
209V	1050–1490	1560	.50	1645	1.8	8.0	26.6
210V	1130–1510	1540	.65	1625	2.0	7.6	29.6
211V	1045–1450	1535	.55	1630	1.6	8.0	22.6
212V	1120–1500	1570	.55	1640	1.4	8.2	24.2
213V	1060–1520	1550	.60	1650	1.7	8.5	18.1
214V	1135–1510	1550	.65	1650	1.5	8.4	22.0
215V	1030–1400	1490	.50	1505	1.2	7.05	35.5
			India kyanite				
Avg.	1098–1468	1504	0.61	1634	2.8	8.6	24.0
High	1270–1535	1540	.80	1730	4.9	9.1	25.0
Low	930–1400	1440	.51	1540	1.0	7.8	23.0

TABLE IX

DATA ON KYANITE-TOPAZ BRICK PRIOR TO LOAD TESTS

Brick No.*	Firing temp. (°C.)	Linear expansion preheat (%)	Wt. standard brick (lb.)	Porosity (% of vol.)
216C	1200	0.6	7.7	30.6
216V	1200	.5	7.7	30.6
217C	1300	.5	7.6	31.1
217V	1300	.4	7.6	30.5
218C	1400	.6	7.6	31.2
218V	1400	.4	7.7	30.2
219C	1500	.3	7.6	30.8
219V	1500	.4	7.6	29.4

*C refers to brick given the modified A.S.T.M. load test; V, to those subjected to the variable-temperature load test.

decrease in the porosity of the refractories as shown in Fig. 12.

The temperatures of the 45-degree tangent in the variable temperature load test are given in Table VIII. All of the brick that contained raw topaz had higher temperatures at the 45-degree tangent than the average of India kyanite brick. The high value for the temperature range of constant maximum expansion of two-thirds of the Bureau of Mines experimental brick exceeded the average of the India kyanite brick. Several of the experimental brick compared favorably in load resistance with the best India kyanite brick.

TABLE X

VARIABLE TEMPERATURE LOAD-TEST RESULTS (MAXIMUM FURNACE TEMPERATURE 1650°C.)

Brick No.	Temp. range of constant max. expansion (°C.)	Temp. 45° tangent (°C.)	Max. expansion hot (%)	Linear shrinkage (%)	Wt. standard brick (lb.)	Porosity (% of vol.)
216V	1050–1420	1485	0.60	5.6	8.0	26.9
217V	1000–1410	1440	0.75	5.1	8.0	26.5
218V	1040–1460	1510	0.60	4.6	7.9	27.2
219V	1035–1460	1540	0.65	2.5	7.8	28.3

TABLE XI

MODIFIED A.S.T.M. CONSTANT-TEMPERATURE LOAD TEST RESULTS (1550°C.)

Brick No.	Shrinkage (%)		Wt. standard brick (lb.)	Porosity, (% of vol.)
	Linear	Volume		
216C	3.6	2.4	7.8	28.7
217C	2.9	2.3	7.7	29.7
218C	2.5	1.8	7.7	30.0
219C	2.4	2.3	7.7	29.7

of the kyanite was added as the raw mineral. Because the dissociation temperature of topaz is much lower than the inversion temperature of kyanite, the kyanite grains remained dense and practically nonporous at the dissociation temperature of the topaz. The vapors from the topaz probably were not absorbed by the raw kyanite to the same extent as with calcined kyanite but reached the surface and formed a highly siliceous glass. Blistering was not noted when calcined kyanite was used instead of the raw mineral.

Brick that contained calcined kyanite with raw topaz had a very low linear expansion in the preheat and an excellent structure. Very good refractories were obtained when a 50–50 mixture of raw and calcined kyanite was combined with raw topaz. Only the last brick of this series that contained 50% raw topaz showed any blisters. Except for the first of this series, which contained 40% of both raw and calcined kyanite, the expansion in the preheat was low.

Figure 11 shows that the weight of a standard-sized brick increased with an increase in the raw kyanite content, whereas calcined kyanite produced a lighter weight refractory. Brick Nos. 202V to 204V, inclusive, contained from 60 to 40% of raw kyanite with raw topaz; they were as heavy as the average of India kyanite brick and had lower porosity. Raw kyanite, as compared with calcined kyanite, caused a marked

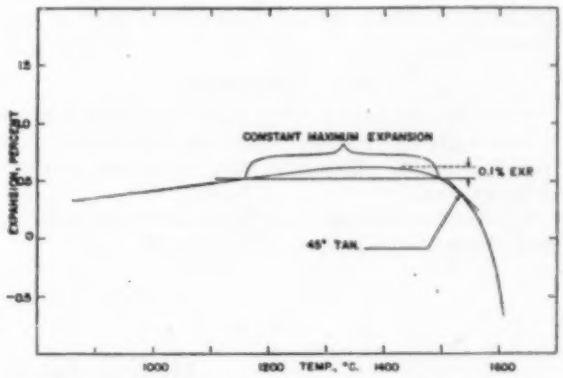


FIG. 13.—Variable temperature load-test results; temperature range of constant maximum expansion within 0.1% limit.

(3) Preheat versus High-Temperature Load Resistance

Preliminary tests have indicated that maximum cold compressive strength was developed by firing kyanite-raw topaz test pieces at 1200°C. Little volume change, moreover, was found between 1200° and 1500°C. These results thus indicate that it might be feasible to produce satisfactory kyanite-topaz refractories by firing them at a moderate temperature rather than at 1500°C., which has been the past laboratory practice. Tests were therefore designed to show the relation of firing temperatures in the preheat to the load resistance of refractories at elevated temperatures.

The body contained 60% −35-mesh calcined kyanite A, 30% −8-mesh raw topaz, and 10% Edgar plastic kaolin. The standard-size brick were pressed at 7400 lb. per sq. in. and were fired 4 hours at the temperatures shown in Table IX, which also gives the linear expan-

sions, porosities, and weights per standard-sized brick after the preheat. The weights and linear expansions showed little change with firing temperatures.

The data for the variable (V) and constant (C) temperature load tests are shown in Tables X and XI. To obtain comparable shrinkage data in the variable-temperature load test, the maximum temperature in these four tests was chosen as 1650°C. With the constant temperature load test (25 lb. per sq. in.), the furnace was raised to 1550°C. in 4½ hours and the temperature was held constant for 1½ hours. The maximum temperature in the A.S.T.M. load test for super-refractories is 1450°C.

The effects of the firing temperatures in the preheat are best shown by the linear shrinkage in both the variable- and constant-temperature load tests inasmuch as the shrinkage decreased with increased preheat firing temperatures. The temperature range of constant maximum expansion and the temperature of the 45-degree tangent with the brick preheated at 1400°C. reached a higher value than with brick preheated at lower temperatures. There was some improvement in the load resistance with the brick preheated at 1500°. The maximum firing temperatures to produce equivalent results, are usually less in commercial firing with the longer soaking period than those used in the laboratory.

VII. Conclusions

When fired at 1500°C., test bars made from kyanite B had a greater volume expansion than those made from kyanite A. The same grain sizes were used for both materials.

The volume expansion of the kyanites became less with a decrease in grain size of the kyanite.

Addition of raw topaz decreased the volume expansion of raw kyanite.

Kyanite retains some of the topaz decomposition products and will absorb such volatiles if heated in close contact with raw topaz. These volatiles may account in part for the bonding action of raw topaz.

There was a marked increase in compressive strength of test pieces containing calcined kyanite and raw topaz fired at 1100°C. as compared with specimens from the same lot fired at 1000°C. The compressive strength reached a maximum of nearly 20,000 lb. per sq. in. with those test pieces fired at 1200°C.

Within the limits of this investigation, all refractories that contained either calcined or raw kyanite with raw topaz had good structures and were well bonded. Very good refractories were produced when a mixture of equal parts of raw and calcined kyanite was combined with raw topaz. One of the best of this class contained 30% each of calcined and raw −35-mesh kyanite A, 30% −8-mesh raw topaz, and 10% Edgar plastic kaolin.

Acknowledgment

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GLOST KILN REFRACTORIES*

By Edward Schramm

Abstract

Saggers for glost placing must give good life and avoid harmful secondary effects on the ware. Low thermal expansion is the most necessary property but, if carried too far, may cause the fault known as pin chipping. This defect, however, is compensated by low expansion in the pin itself. The system sagger–pin–ware should be adjusted to minimize tensile stresses in cooling.

I. Introduction

Refractories for use in glost kilns must be considered from two aspects, namely, (1) their adequacy to perform the service for which they are intended, including the requirement to give satisfactory life, and (2) their freedom from the tendency to cause harmful secondary effects on the product. Among these secondary effects, which are the chief subject of the present discussion, may be included sagger dirt or kiln dirt and pin chipping; the latter is a common fault in firing flat tableware onpins.

In biscuit kiln practice, heavy loads are carried on the sagger bottoms; temperatures may be quite high, but firing schedules are normally slow; these conditions combine to place the chief emphasis on refractoriness or the ability to carry load at high temperatures without slumping or cracking. In glost kiln practice, however, the question of refractoriness is secondary; firing schedules are faster and the factor determining the life of refractories is their resistance to heat shock.

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II. Relation Between Structure and Performance

Heat-shock resistance is influenced by structural characteristics, such as the proportioning and sizing of the grog and by certain basic physical properties, especially thermal expansion and thermal conductivity, which determine the extent of the stresses produced by rapid temperature change. Working with structural factors only, the optimum result is obtained with bodies of high grog content and a rather coarse grading of the grog. This method of increasing life yields a friable sagger, which is the source of much dirt contamination. The damage may occur in placing the ware in the sagger, in placing the saggers in bungs, or by spitting out in the fire. As a result, there is a gradual deterioration of the sagger top to a point where good closures cannot be obtained.

If, because of these effects, it is decided to sacrifice sagger life to protect the product by making a denser, finer-structured sagger, it is soon found that a vicious circle is being followed. The saggers crack from heat shock, and the opening permits access of dust from the kiln atmosphere, which may be more damaging than the sagger dirt itself.

Certain special refractories, notably silicon carbide, possess remarkable heat-shock resistance as a result of their high thermal conductivity, but such refractories are not generally applicable to glost placing. The most helpful approach is to work for refractories of low thermal expansion. The general introduction of talc into sagger mixes has accomplished this purpose and has produced saggers satisfactory for both life and cleanness. The best development along these lines is probably represented by the cast refractories on the market, which afford a combination of tight structure, low expansivity, and thin wall section.

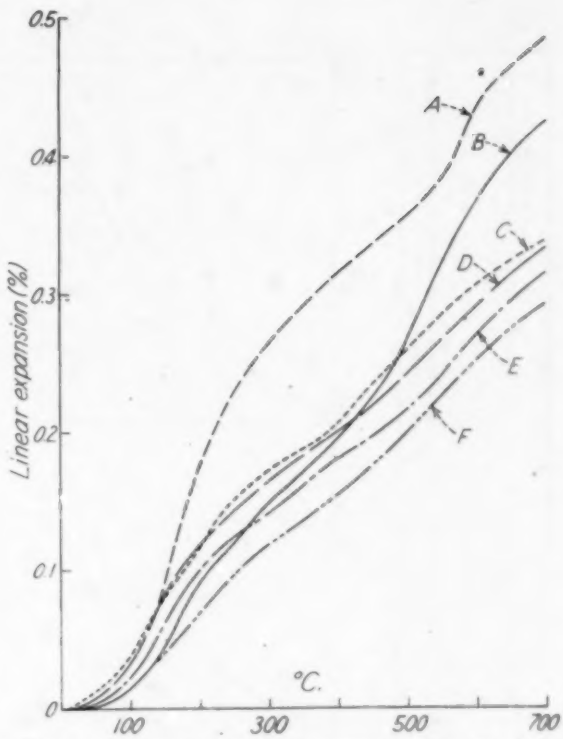

Fig. 1.—Curves: *A*, cone 13 sagger, no talc; *B*, china body; *C*, 2.5% talc sagger; *D*, 5.0% talc sagger; *E*, 7.5% talc sagger; and *F*, cast sagger.

III. Pin Chipping

During the indicated course of development, a most disturbing complication was encountered, namely, a sharp increase in the amount of pin-chipped ware. As a sagger of ware cools, a tensile stress develops at the pin support, which under certain conditions pulls a fragment out of the body, leaving unsightly holes in the back of the leaf. The history of this occurrence indicated that the tensile stresses at the pin increased as the thermal expansion of the sagger was lowered, and later consideration of the phenomenon pointed to the same conclusion.

In a sagger loaded with pinned ware, the pin must be considered to be rigidly attached to the sagger because the weight of the piece of ware holds it in position. After cooling, if the sagger has a higher coefficient than that of the ware (more contraction), the stress at the support will be compressive and no harm will be done. In the theoretical case of identical contraction, no stresses develop; in the actual case of lower contraction of the sagger, a tensile stress develops that is proportional to the difference in contraction between the ware and the sagger. In the preceding simplified analysis, the expansivity of the pin itself has been neglected, but this point will be covered in the more detailed discussion to follow.

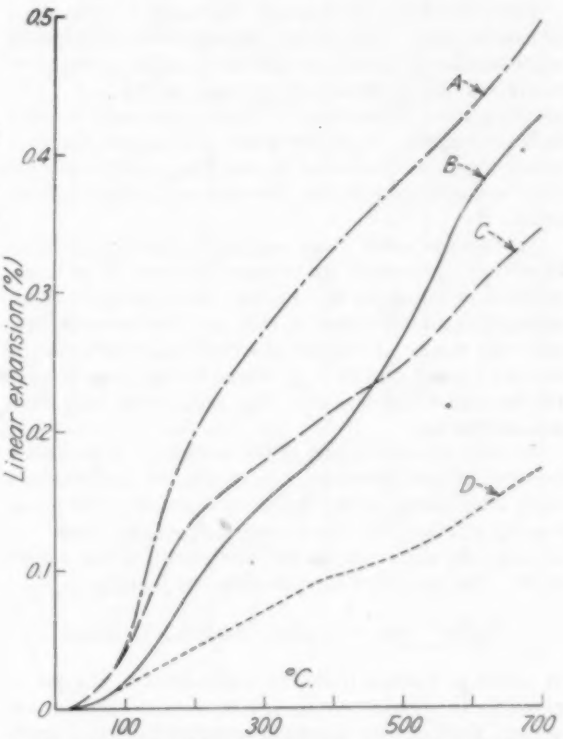

Fig. 2.—Curve *B*, china body; curves *A*, *C*, and *D*, refractory bases.

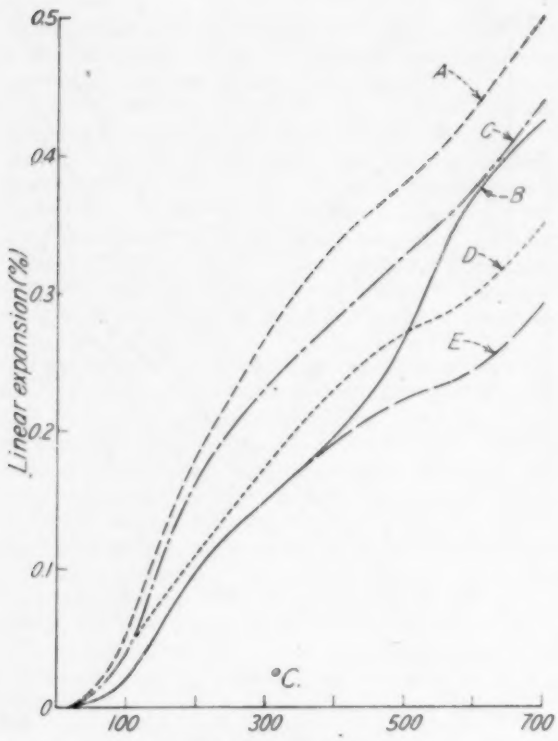

Fig. 3.—Curves: *B*, china body; *A* and *C*, clay pins; *D*, pin C plus 10% talc; *E*, pin C plus 15% talc.

The first efforts to alleviate this trouble were along structural lines. Thus, if the pin body were deliberately made weaker, it should be possible to reach a condition where the pin rather than the ware would fail. This possibility was demonstrated, but the solution proved to be inadmissible. Such pins would not support the ware unless they were increased in size to a considerable extent, and any move in that direction involved reduction in fill.

Another approach was to attempt a less rigid manner of setting. Pins were set to meet the ware at an acute angle both in sagger and in open-rack placing. Some mitigation was obtained in this way, but no complete cure was made. A related observation in rack placing showed a much greater tendency to pin chipping toward the bottom of the rack near the supporting base than toward the top.

Because the pin is part of the system, it is necessary to consider how to treat it. As mentioned previously, a rigid attachment to the sagger is assumed. The pin in cooling will therefore move toward the sagger, that is, in an opposite direction to the movement of the sagger itself. The net effect is represented by formula (1).

$$\text{Sagger} - \text{pin} = \text{ware for condition of no stress} \qquad (1)$$

It therefore follows that any adjustment of the pin in expansivity should be opposite in sense to that of the sagger, that is, the favorable combination is a high-expansion sagger and low-expansion pin.

Inasmuch as this problem involves securing a fit between ware and refractories, a study of the expansivity of each was undertaken. The results are shown in three sets of curves, the curve for the ware being repeated in each set. Figure 1 shows the data for various types of saggers, namely, a cone 13 biscuit sagger with no talc, a glost sagger containing 2.5, 5.0, and 7.5% talc, and a commercial cast sagger. Figure 2 shows the curves for various bases used for open-rack placing. Figure 3 shows curves for the various pin bodies, namely, *A*, a commercial pin; *C*, a clay pin with no talc; *D*, a pin with 10% talc added to body C; and *E*, a pin with 15% talc added to body C.

In Fig. 1, the cone 13 biscuit sagger mix with no talc has an expansivity greater than that of the body. When this mix was used to make glost saggers, pin chipping was eliminated but the saggers were unsatisfactory in life and cleanliness.

Curve *D* in Fig. 1, the standard glost sagger with 5% talc, and curve *A* in Fig. 3, which represents a commercial clay pin with no talc, were a bad combination and gave pin chipping. Curve *C* in Fig. 3 is a clay-pin mix with somewhat lower expansion; curves *D* and *E* give the effect of adding 10 and 15% talc, respectively, to pin C. The combination of curve *D*, Fig. 1, the sagger with 5% talc, with the pin represented by curve *E* in Fig. 3 afforded a solution of the pin problem without sacrificing other necessary qualities in the sagger. A limitation, however, still exists to the extent to which the expansivity of a glost sagger can be reduced. Saggers were made of a body in which the talc was increased to 10%. Bad pin chipping resulted, even with the improved pins.

Figure 2 shows curves for the refractory bases for open-rack placing, which yielded results similar to those of the saggers. Base *A* was unsatisfactory because of cracking; *D* showed bad pin chipping; and *C*, in conjunction with pin *E*, yielded good results.

It may seem remarkable that a short element like the pin should have so marked effect, but a brief calculation will make this clear. A system is assumed for a sagger with an 11-in. linear section, a 3-in. pin length, and an 8-in. ware length between the pin supports. The stress at the pin supports is then given by formula (2).

$$\text{Contraction of 8-in. ware} - \text{11-in. sagger} + \text{3-in. pin} \qquad (2)$$

Using the appropriate values from 700° taken from the curves for the body and 5% talc sagger, the following results are obtained:

$$\text{Pin A} = 0.0340 - 0.0374 + 0.0150 = 0.0116$$
$$\text{Pin E} = 0.0340 - 0.0374 + 0.0088 = 0.0054$$

The change in the pin reduces the stress by more than 50% although it does not entirely eliminate the tension. For this reason, as already noted, it proved impossible to lower the expansion of the sagger any more. The refractories found suitable have a mean coefficient from 700°C. for the sagger of 4.86×10^{-6} and for the pin, of 4.14×10^{-6}.

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